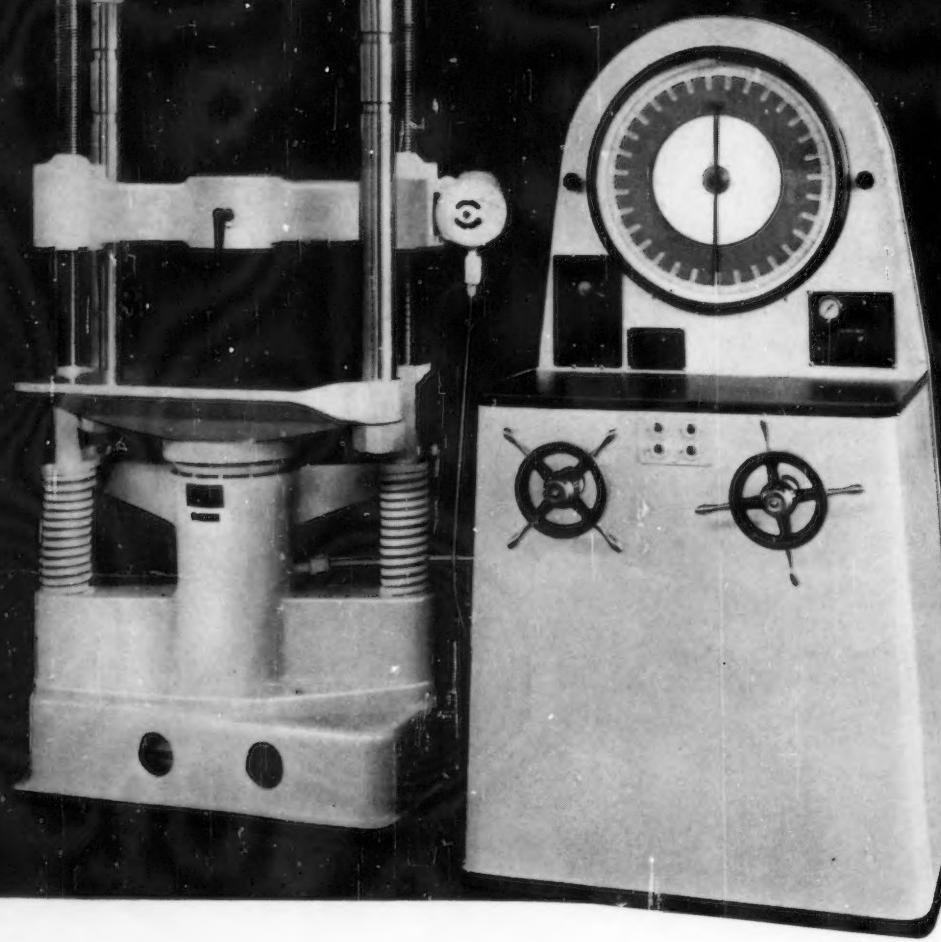


# ACTM Bulletin

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# ASTM BULLETIN

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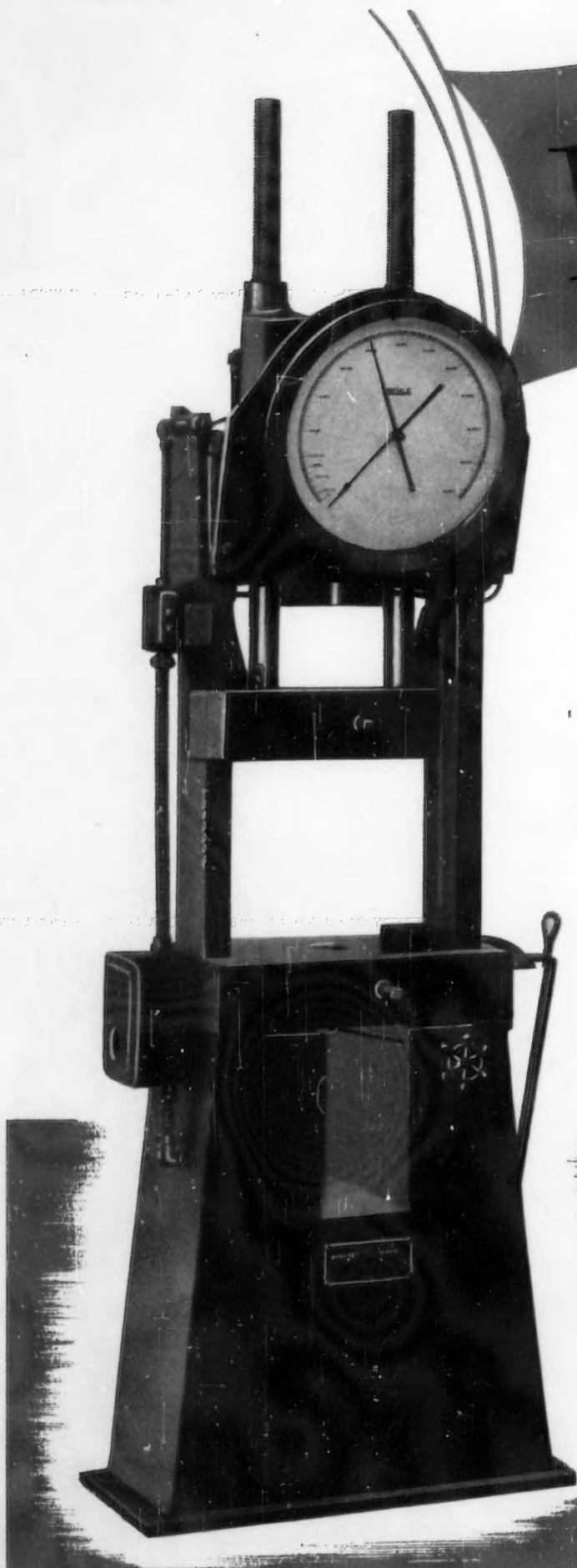
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## JANUARY—1941

No. 108



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"Promotion of Knowledge of Materials of Engineering and Standardization of Specifications and Methods of Testing"

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Number 108

January, 1941

## Spring Meeting and Committee Week in Washington During Week of March 3

### Sessions on Color and Particle Size Measurements Scheduled

As previously announced, two technical symposiums, one on New Methods for Particle Size Determination in the Subsieve Range, the other on Color—Its Specification and Use in Evaluating the Appearance of Materials, will be the features of the Society's Spring Meeting to be held at The Mayflower in Washington, on March 4 and 5. The two sessions comprising the Particle Size Symposium are scheduled for Tuesday afternoon and

evening, March 4, and the Symposium on Color will be on Wednesday afternoon.

This latter feature is sponsored jointly by the Inter-Society Color Council and A.S.T.M. The Council is holding its Tenth Annual Meeting on March 4 and 5, and on the evening of Wednesday, a session entitled "Parade of Color" is to be held, to which all A.S.T.M. members and committee members are invited.

Details of these sessions appear in the following pages.



The Heart of the Nation from the East

*Fairchild Aerial Survey; Capt. A. E. Nesbitt*

A.S.T.M. Committee Week, which has become an annual event, will also be held from Monday, March 3, through Friday, with meetings of standing committees, subcommittees, and sections on all five days. A detailed schedule of committee meetings will be mailed in February to the members of each committee that is meeting. There will be available at the A.S.T.M. registration desk at The Mayflower a final schedule complete with room assignments.

The Washington Committee on Arrangements, headed by Vice-President G. E. F. Lundell, Chief, Chemistry Division, National Bureau of Standards, with H. S. Rawdon, of the Bureau, serving as *Secretary*, consists of the following members: T. I. Coe, W. E. Emley, A. C. Fieldner, H. A. Gardner, F. H. Jackson, G. F. Jenks, and Stanton Walker.

This committee has decided not to sponsor a formal dinner during the meetings, or to set up a definite schedule of entertainment, trips, and plant visitations, but it will have available during the meeting detailed information concerning points of interest and will endeavor through representatives to be of service to the committee members who will be in Washington.

#### TECHNICAL SYMPOSIA

Full details of the two technical symposiums featuring the Spring Meeting are given in this BULLETIN and abstracts of the papers are also published to stimulate participation. In addition to the authors of the papers, who are technical authorities in these fields, a number of other engineers and technical men will be asked to contribute discussion. This is always one of the most interesting features of an A.S.T.M. symposium.

Each of these topics is one of much significance and of great importance to specific industries.

#### Tenth Annual Meeting of Color Council, Washington, March 4 and 5

ON MARCH 4 AND 5 IN Washington, the Inter-Society Color Council will hold its Tenth Annual Meeting in which there is included as one session the Symposium on Color—Its Specification and Use in Evaluating the Appearance of Materials, being sponsored jointly by the A.S.T.M. and the I.S.C.C.

A preliminary program for the Color Council meeting has been developed and is published here. Final details of this program will be announced later, but if further information is desired, it can be obtained from the secretary of the Inter-Society Color Council, Box 155, Benjamin Franklin Station, Washington, D. C.

#### PRELIMINARY PROGRAM FOR I.S.C.C. MEETING

March 4

- 9:30 a.m. Discussion Session: Forrest Lee Dimmick, Chairman.  
(At American Pharmaceutical Assn. Headquarters, 2215 Constitution Ave.)
- 2:00 p.m. Annual Business Session: Deane B. Judd, Chairman.  
Reports of committees, and of chairmen of delegations from member bodies.  
(At American Pharmaceutical Assn. Headquarters.)
- 6:30 p.m. Informal Dinner for delegates and members.

A cordial invitation to attend is extended to all those interested.

#### COMMITTEE MEETINGS

More than the usual number of standing committees have signified their intention of participating in Committee Week. The groups which thus far plan to meet in Washington include the following:

A-1 on Steel	D-3 on Gaseous Fuels
A-2 on Wrought Iron	D-4 on Road and Paving Materials
A-3 on Cast Iron	D-5 on Coal and Coke
A-5 on Corrosion of Iron and Steel	D-6 on Paper and Paper Products
A-7 on Malleable Iron Castings	D-8 on Bituminous Waterproofing and Roofing Materials
A-10 on Iron-Chromium, Iron-Chromium-Nickel and Related Alloys	D-9 on Electrical Insulating Materials (Wardman-Park Hotel)
B-3 on Corrosion of Non-Ferrous Metals and Alloys	D-11 on Rubber Products
B-5 on Copper and Copper Alloys, Cast and Wrought	D-13 on Textile Materials
B-6 on Die-Cast Metals and Alloys	D-20 on Plastics (Wardman-Park Hotel)
B-7 on Light Metals and Alloys, Cast and Wrought	Technical Committees and Sections of Committee E-1 on Methods of Testing
C-5 on Fire Tests of Materials and Construction	Sub. A-2 of E-3 on Chemical Analysis of Metals
C-8 on Refractories	E-9 on Research
C-9 on Concrete and Concrete Aggregates	Joint Committee on Definitions of Terms Relating to Heat Treatment
C-15 on Manufactured Masonry Units	Organization Meeting of Committee on Electrodeposited Metallic Coatings
C-16 on Thermal Insulating Materials	A.S.A. Sectional Committee C59 on Electrical Insulating Materials
D-1 on Paint, Varnish, Lacquer, and Related Products	

It should be noted that a number of other committees may decide to participate; full information will be mailed to each committee member in February.

March 5

2:00 p.m. Joint A.S.T.M.-I.S.C.C. Technical Session: A Symposium on Color—Its Specification and Use in Evaluating the Appearance of Materials: M. Rea Paul, Chairman.  
A detailed announcement of this symposium is published on another page of this BULLETIN.  
(At the Mayflower Hotel.)

8:00 p.m. Popular Session: Parade of Color: William D. Appel, Chairman.

A.S.T.M. members will join the I.S.C.C. for this session. The meeting is to be held in the auditorium of the Potomac Electric Power Co., 10th and E Sts., N. W., the usual meeting place of the Washington-Baltimore branch of the Illuminating Engineering Society, which, with the Washington Colorists, is also joining the I.S.C.C. for this session.

TRENDS IN COLOR PHOTOGRAPHY—Earl A. Trager, Manager, Washington Branch, Bell & Howell Co., formerly Chief Naturalist, National Park Service.

PAINT STYLING DEMONSTRATION—National Paint, Varnish & Lacquer Assn., by prominent members of their Council on Paint Styling, which keeps its finger on the color pulse of the Nation.

EXPLORING THE MAGIC WORLD OF COLOR—Herbert Thompson Strong, A spectacular and thrilling presentation by the "World's Greatest Color Magician."

# Symposium on New Methods for Particle Size Determinations in the Subsieve Range

## A Technical Feature of Spring Meeting in Washington, on March 4

THE HOLDING OF two technical symposiums at the Spring Meeting of the Society to be held in Washington on Tuesday and Wednesday, March 4 and 5, while not an innovation, because dual symposiums have been held previously, nevertheless focuses attention on the importance of this meeting as a technical forum for the discussion of topics of much concern to the field of engineering materials. The Symposium on New Methods for Particle Size Determinations in the Subsieve Range, being held in two sessions on the afternoon and evening of Tuesday, March 4, will be of concern to a large number of industries. The Symposium on Color, being held on the afternoon of the following day, is likewise of widespread interest.

While there have been discussions on particle size measurement at A.S.T.M. meetings, and a number of papers on this subject have appeared in the *Proceedings*, there has been no complete session devoted entirely to this subject. It has been evident for some time that with a number of significant new developments and the growing importance of the subject to many industries, a symposium would serve a very useful purpose and this fact has been definitely kept in mind by Mr. C. E. Bennett, of the New Jersey Zinc Co., who is chairman of the committee responsible for the Washington Symposium.

In connection with the inter-relation of the Symposia on Color and on Particle Size, there will be a number of those attending the Spring Meeting who are concerned with both topics. This is perhaps particularly true in the field of pigments. It is of interest to note that the first paper presented before the A.S.T.M., dealing with the question of particle size entitled "The Classification of Fine Particles According to Size," was given at the Society's 1910 annual meeting by Dr. G. W. Thompson, whose 1923 paper on color is referred to in the accompanying statement on the Symposium on Color. In his paper Doctor Thompson showed some very interesting photomicrographs of classified white lead, red lead, portland cement and barytes. There were not many other technical papers on this general subject for many years, but in 1928

Dr. L. T. Work, then Instructor in Chemical Engineering, Columbia University, now Director of Research and Development, Metal and Thermit Corp., and who for years has been very active in this field and serves as chairman of Technical Committee III on Particle Size and Shape of Committee E-1 on Methods of Testing, presented a very extensive paper dealing with "Methods of Particle Size Determination." In this he noted the aims in fineness measurement of ground minerals, pigments, fuels, and cements, and classifies various tests according to direct measurement and indirect comparison. Doctor Work pointed out that special characteristics of fineness might be stressed in each of the various fields covered. In the case of pulverized coal, for instance, extreme fines were very desirable and requirements for pigments were diverse. The most significant factors were a minimum of coarse material desired for smooth texture and a definite amount of surface for its relation both to wetting by the vehicle and to the hiding or covering power of the paint.

A definite impetus was given to the question of fineness measurement, surface area of fine particles, etc., in the field of cement, when it was realized that the subsieve elements exerted such an important influence. There have been a number of papers describing various instruments and methods of procedure including the Wagner turbidimeter which was described by Mr. Wagner in his paper at the 1933 annual meeting. This procedure, since published as an A.S.T.M. tentative method of test, covers the fineness of portland cement as represented by specific surface expressed as total surface area in square centimeters per gram of cement.

Latest developments in particle size measurement will be covered in the symposium which is to comprise seven papers. It will be noted from the list which follows that absorption methods, permeability methods, sedimentation methods, and correlation of particle size measurements will be covered and that the widely publicized electron microscope is to be described with emphasis on its practical applications in this field.

## Abstracts of Technical Papers Comprising the Symposium on New Methods for Particle Size Determinations in the Subsieve Range

### SYMPOSIUM ON NEW METHODS FOR PARTICLE SIZE DETERMINATIONS IN THE SUBSIEVE RANGE

A New Method for Measuring the Surface Areas of Finely Divided Materials and Its Use in Determining the Size of Particles—P. H. Emmett, Department of Chemical Engineering, Johns Hopkins University.

The Adsorption of Pigments—W. W. Ewing, Department of Physical Chemistry, Lehigh University.

The Determination of Subsieve Particle Size Distributions by Sedimentation Methods—S. W. Martin, Research Laboratory, National Lead Co.

The Shape and Surface of Fine Powders by the Permeability Method—P. C. Carman, University of Capetown.

Methods for Determining Particle Size Distribution—Lincoln T. Work, Director of Research and Development, Metal and Thermit Corp.; and Herbert E. Schweyer, Columbia University.

Surface Area of Portland Cement—P. S. Roller, Physical Chemist, Eastern Experiment Station, U. S. Bureau of Mines; and P. V. Roundy, Jr., Cooperative Fellow, American Instrument Co.

RCA Electron Microscope—James Hillier, Research Laboratories, RCA Manufacturing Co.

Abstracts of the technical papers follow on the next page.

## General Statement

THE DEVELOPMENT of satisfactory, practical test methods for the determination of particle sizes depends upon the research of individual investigators. In the past few years a number of people have been active in this field and the purpose of this symposium is to draw wider attention to their work and consideration of the Society to those methods which appear to have possibilities as standard methods. The methods described will cover the determination of particle sizes from the colloidal range

up to sieve sizes. Two papers are devoted to adsorption methods, one to the permeability method which is just coming into extensive application in this country, one to sedimentation methods, and two papers will discuss the correlation of particle size measurements. The paper by Mr. Hillier on the electron microscope will be of special interest since it will describe practical applications of an instrument which is simple and rugged enough for general laboratory use.

C. E. Barnett

### A New Method for Measuring the Surface Areas of Finely Divided Materials and Its Use in Determining the Size of Particles

By P. H. Emmett

WITHIN THE PAST five years a new method has been worked out for measuring the surface area of finely divided or porous solids by the use of low temperature adsorption isotherms. This method applied to non-porous materials affords an additional means of obtaining values for the average particle size of a substance.

The surface area measurements depend upon making adsorption isotherms of some gas such as nitrogen near its boiling point and then selecting on the isotherm the volume of gas corresponding to a monolayer. A simple multiplication of the number of molecules in such a monolayer by the average cross-sectional area of the molecules yields a value for the surface area. Details of the apparatus and procedure, including the application of a theoretically derived equation for estimating the volume of adsorbed gas in the monolayer, have been fully described in the literature. Application of the method to several hundred miscellaneous materials, and comparison of our results wherever possible with those obtained by other means, has continued to strengthen our confidence

in its reliability and reproducibility.

The calculation of the average particle size of a finely divided nonporous material from the surface area obtained by this gas adsorption method entails the same types of uncertainty due to shape factors and methods of averaging that are involved in any method for estimating particle diameters from measurements of the total surface area of the particles. In addition, the proposed method has the following limitations as applied to measuring particle size: (1) it cannot be applied to porous materials; (2) the surface area of a 25-cc. sample of a powdered substance must be as large as about 10,000 sq. cm. if the results are to be reproducible to 5 per cent. On the other hand, the method has the advantage of being applicable to particle sizes too small to measure by any other method. Excellent agreement with the direct microscopic method has been obtained on sized glass beads 5 microns in diameter and with the ultra-microscopic particle count method as applied to zinc oxide pigments in the 0.1 to 0.3-micron range.

### The Adsorption of Pigments

By W. W. Ewing

THE SPECIFIC SURFACE of pigments can be determined by adsorbing wetting agents on the surface from solutions. This entails (1) the selection of a solute which is preferentially adsorbed on the pigment; (2) the selection of the correct solvent; (3) the preparation of the pigment surface; and (4) a knowledge of the cross-sec-

tional area of the adsorbed molecule in its oriented position. Successful experiments have been carried out on various zinc oxide pigments using anhydrous benzene as the solvent and methyl stearate and ethylenedipalmitate as the adsorbents.

### The Determination of Subsieve Particle Size Distributions by Sedimentation Methods

By S. W. Martin

THE INFORMATION AVAILABLE in the literature on the determination of subsieve particle size distributions is examined for solid-liquid systems in terms of two fundamental principles, namely, (1) the cumulative settling law for a polydisperse material, (2) Stokes' frictional resistance law for a moving spherical particle. On the basis of the cumulative settling law, gravitational and centrifugal sedimentation procedures are classified

into cumulative, accurate incremental, and approximate incremental methods. The theory underlying each category is considered and literature citations are made for purposes of illustration and confirmation of particle size distribution values which are obtainable from sedimentation methods. Finally, the inherent advantages, as well as restrictions which must be imposed for valid results, are critically evaluated.

### The Shape and Surface of Fine Powders by the Permeability Method

By P. C. Carman

THE THEORY OF THE permeability method and details of experiments to test its validity have been fully discussed in previous papers. In the present paper, this

previous work is summarized in a few words, the main function of the paper being to give a full description of the experimental technique, to discuss the limitations of the

method, and to present new data relating to the shape of nonspherical particles. While the present experimental evidence is inconclusive, it would appear that the method

tends to give somewhat high values of the specific surface for very fine particles, particularly for very heterodisperse powders extending down to colloidal dimensions.

### Methods for Determining Particle Size Distribution

By Lincoln T. Work and Herbert E. Schweyer

A CRITICAL REVIEW is given of methods proposed for determining the size distribution of polydisperse materials of such size that the majority of the particles are above the colloidal range. As a guide to the selection of a

method for a particular purpose, a summary is given and means of representing the data are discussed. A table of nomenclature is included.

### Surface Area of Portland Cement<sup>1</sup>

By Paul S. Roller and P. V. Roundy, Jr.

THE SIZE DISTRIBUTION of several portland cements was determined by an absolute method involving use of a particle size air analyzer; and from the data, surface area was calculated by a statistical procedure. Determinations on the same cements were also made by the Wagner turbidimeter and by an air permeability method after Gooden and Smith. In the latter method the conversion factor to a smooth cube particle was ascer-

tained by testing several cement fractions. Surface areas obtained by the various methods were compared and discussed. Size constants other than surface area, such as coefficients of uniformity and regression, which are obtained only from distribution data, have been considered, and simplified methods of calculations indicated.

<sup>1</sup> Published by permission of the Director, U. S. Bureau of Mines.

### RCA Electron Microscope

By James Hillier

THE USEFUL MAGNIFICATION of microscopes, using visible or ultraviolet light is limited to about 3000 diameters, due to the relatively long wave length of the observing medium. High velocity electrons, which have an extremely short effective wave length, can, with the aid of electron optics, be used in an electron microscope to obtain magnifications that are about 100 times greater than those obtained with a light microscope.

The electron microscope embodies principles similar to those employed in an optical microscope, with magnetic electron lenses taking the place of glass lenses. An elec-

tron microscope capable of very high resolution and suitable for general laboratory use has been built in the RCA laboratories. This instrument is rugged, simple to operate, and completely self-contained. Specially designed power supplies provide the extremely constant voltage and current supplies required for its operation.

This new microscope, which is capable of resolving detail finer than 50 Å, finds extensive applications in almost every field of science, and should be an invaluable adjunct to any industrial or scientific research laboratory.

## A Symposium on Color—Its Specification and Use in Evaluating the Appearance of Materials

### A Technical Feature of Spring Meeting in Washington, on March 5

To MARK TWAIN is attributed the remark that everybody talks about the weather, but no one does anything about it. In one respect this comment about the weather might apply to color, because a great many people consciously or unconsciously talk and think quite a bit about it. But here the parallel ceases, for quite a large number of people are doing something about color, and a number of organizations and groups are concerned primarily with it—in particular, one group known as the Inter-Society Color Council, which jointly with A.S.T.M. is sponsoring a Symposium on Color—Its Specification and Use in Evaluating the Appearance of Materials. This symposium, comprising six technical papers, will be one of the technical features of the Spring Meeting of the American Society for Testing Materials, being held in Washington during the week beginning March 3. The Color Symposium is scheduled for Wednesday afternoon, March 5, at The Mayflower Hotel. It will be preceded

on Tuesday afternoon and evening by a Symposium on New Methods for Particle Size Determinations in the Subsieve Range, for details of which see another page of this BULLETIN.

If one thinks even for a few moments about color, it is amazing to realize what an important part color plays in our daily life and also our industrial activities. Selections of color for apparel are daily routine for almost everyone; the appearance of much of the food we eat which comes down basically to color; whether the sky is blue or gray—these are other everyday factors with which color is involved. To the home owner color is constantly to the fore: in determining the color of paint for his home, type of wall paper or wall finish, color of rugs, furniture, curtains, and the like.

Industrially color is extremely important because there have been a number of authoritative studies indicating the effect of color on efficiency, and coming "home" to

the field of engineering materials color is an extremely important factor in connection with the inspection or determination of quality of many products. One could go on at length citing examples of different points in connection with color. There is hardly any field of human activity in which color is not more or less a factor.

#### WIDE ACTIVITY IN THE FIELD OF COLOR

In addition to the Inter-Society Color Council, which comprises some 75 delegates appointed by its dozen member societies or bodies, and in addition some 75 individual members, there are a number of other associations and groups whose activities are almost entirely confined to that of color. Then there are other groups such as the Optical Society of America, the American Physical Society, Technical Association of the Pulp and Paper Industry, and the American Society for Testing Materials, many of whose activities concern the field of color. Each of the groups mentioned is a member body of the Inter-Society Color Council, the number of delegates appointed depending upon the range and diverse character of its work. The Color Council sponsors meetings with its member societies, and its Proceedings are usually published in the journals of these societies. One of the important activities of the Inter-Society Color Council is its News Letter to its members.

In the short article entitled "How Many Reds Can He See When Man Bites Dog?" the editor of the News Letter points out that a leading metropolitan daily was not exaggerating when it reported that about two million colors could be distinguished by the normal human eye. As a matter of fact, the National Bureau of Standards has stated that at least ten million can be discriminated by the normal (not color blind) human being.

A number of publications deal with the psychological, emotional, or therapeutic effects of color. A relatively recent issue of a widely distributed popular magazine included an article on the therapeutic effects of color, in which it is indicated that the wearing of red makes a man feel strong and dynamic; yellow, gay; blue soothes him, and green is apt to make him amorous.

#### COLOR IN THE A.S.T.M.

While color must have had some consideration in the earlier years of the Society's work, apparently the first formal paper on this subject was presented in 1914 by I. G. Priest dealing with a Supplementary Report on Color of Turpentine. Since then there have been a number of important contributions in this field, many dealing with methods of determining color, and instruments used. The development of a system of color measurement has been a very important problem and in 1922 there was a paper on this subject by H. S. Busby.

There have been a number of very interesting contributions to the Society's *Proceedings* on the subject and in 1923 Past-President and Honorary Member G. W. Thompson, then Chief Chemist, National Lead Co., presented a very interesting paper dealing with classification of colors, relation of achromatic colors, etc., and among other things he quoted the then A.S.T.M. definition of color, which, it is very interesting to note, is still the official definition as given in the Definition of Terms Relating to Paint, Varnish, Lacquer, and Related Products (D 16-40 T) as follows:

*Color.*—A generic term referring inclusively to all of the colors of the spectrum, white and black, and all tints, shades, and hues which may be produced by their admixture.

Color involves a definite effect produced by the action of light upon the retina of the eye dependent upon the optical composition of the light. This term is also used in reference to material substances such as pigments, stains, dyes, etc., but in specifications it should be recognized that color is primarily a physiological sensation.

The importance of color received increasing recognition, and the Fifth Edgar Marburg Lecture, delivered in 1930 by C. E. Kenneth Mees, of Eastman Kodak Co., concerned "Color and Its Measurement" in which he discussed the physical nature of color and the methods which can be used for its measurement and standardization. It is of interest to quote the closing two paragraphs of Doctor Mees' Lecture:

"The commercial use of colorimetry is still in its infancy, and it still presents serious difficulties. The application of colorimetric methods to each industrial problem generally requires a special study, and there is at present a dearth of industrial scientific men qualified to undertake this work. Nevertheless, the standardization of color is of an importance which increases daily. The purchasers of colored goods are insisting more and more on stability, constancy, and repeatability of color."

"In this lecture, I have been able to do no more than indicate the principles of the subject, but I am convinced that within a few years the measurement of color, both analytically by means of the spectrophotometer and synthetically by means of various forms of colorimeters, will increase and will form by no means a negligible part of the work of laboratories devoted to the testing of materials."

Just about a decade has elapsed since Doctor Mees delivered his Lecture, and the symposium to be held in Washington, on March 5, 1941, will certainly indicate tremendous development in the commercial use of colorimetry and, of course, will stress a number of very important industrial problems in connection with the specifying of color and its use in evaluating the appearance of materials.

The fact that the Society has five representatives on the Inter-Society Color Council who are active in the work of various standing committees indicates the interest of A.S.T.M. in this field and it cordially welcomes the participation of the I.S.C.C. in sponsoring jointly this symposium. At least 17 of the Society's specifications and tests pertain to color or the colorimetric test, and this number will undoubtedly increase rapidly in the coming year.

#### THE SYMPOSIUM ON COLOR

This symposium was developed by a joint committee headed by M. Rea Paul, National Lead Co., including the following members:

A. G. Ashcroft	R. S. Hunter
W. E. Emley	D. B. Judd
C. E. Foss	A. W. Kenney
W. R. Fuller	Paul Rapp
H. A. Gardner	W. M. Scott

The symposium will be based on the following technical papers, abstracts of which are given below. Each of the authors of the papers has specialized for years in this particular field and the final publication which in addition to these papers will include oral and written discussion will undoubtedly be of great value to all those concerned with color, particularly as it involves the specific phase being discussed.

# Abstracts of Technical Papers Comprising the Symposium on Color—Its Specifications and Use in Evaluating the Appearance of Materials

To be held at The Mayflower, Washington, D. C. on Wednesday afternoon, March 5. The papers and discussions will subsequently be published in a special volume.

Introduction to Color—Deane B. Judd, Physicist, National Bureau of Standards.

Color of Transparent Materials—Francis Scofield, Chemist, National Paint, Varnish, and Lacquer Assn., Inc.

Hiding Power and Opacity—R. H. Sawyer, Krebs Pigment and Color Corp.

Color Standards for Opaque Materials—I. H. Godlove, E. I. du Pont de Nemours and Co.

The Spectrophotometer in the Determination of the Color of Materials—A. E. Parker, Electrical Testing Laboratories.

Photoelectric Colorimetry—Richard S. Hunter, Junior Physicist, National Bureau of Standards.

## Introduction to Color

By Deane B. Judd

COLOR IS AN ASPECT of the appearance of objects and lights dependent upon the spectral composition of the light reaching the retina of the eye and upon its temporal and spatial distribution. *Black, white, and gray* are colors as well as *red, yellow, green, blue, purple*, and their intermediates. The colors of objects have three attributes: hue, lightness, and saturation. *Hue* is the attribute by which we tell whether the color is red, yellow, green, blue, purple, or an intermediate. *Lightness* is the attribute by which we distinguish a light object color from a dark one. For every object color possessing a hue there is a gray of the same lightness, called the *equivalent gray*. *Saturation* is the degree of difference between the chromatic color and its equivalent gray. The object-color solid is obtained by plotting lightness as distance upward from a base plane, hue according to angle about a vertical axis, and saturation as distance from this axis.

Opaque objects appear to have color only on their surfaces. The solid representing surface colors shows black at the bottom of the central axis with the intermediate grays ranging uniformly upward to white at the top. Transparent objects (plastics, glasses, crystals) and media (dye solutions, oils, paint vehicles) appear to have color through and through them. The central axis of the solid representing the colors of transparent objects and media shows black at the bottom with lighter colors ranging upward to the color known paradoxically as *colorless*.

By means of these diagrammatic solids, it is possible to simplify thinking about color. Terms commonly used to describe the character of color differences find their most succinct definition by reference to these solid figures. It is possible and convenient to describe the character of any color difference by the terms *red, yellow, green, blue, light, dark, weak* (less saturated), and *strong* (more saturated); other color terms, such as pale, deep, clean, muddy, blacker, and whiter, refer to methods of specifying points in the object-color solids alternate to the hue-lightness-saturation method. These diagrammatic solids refer only to the appearance of objects, and it is not possible to determine by physical measurement of an object exactly what point in the solid represents its color; we can only specify it by a point in some psychophysical color system which correlates more or less closely with the purely psychological arrangement given by the object-color solid.

The physical characteristic of an object which determines its color under usual viewing conditions is its power to change the spectral and angular composition of the

radiant energy incident upon it. An instrument for comparing in spectral composition the radiant energy leaving an object with that incident upon it is called a *spectrophotometer*; this instrument yields primary information relative to color and is used in the A.S.T.M. specification for spectral apparent reflectivity for paints. An instrument for determining the angular distribution of radiant energy leaving an object is called a *goniophotometer*; this instrument yields primary information relative to glossiness and transparency which are aspects of appearance so closely associated with color that it is often easiest to deal with them together. These instruments are used to analyze both reflected and transmitted radiant energy; hence they apply to any object whether it be transparent, translucent, or opaque.

By the use of an illuminant of standard spectral and angular distribution, object colors may be specified simply by paying attention to the reflected or transmitted radiant energy which leaves the object. It has been found possible to color match any beam of radiant energy by a mixture in suitable proportion of three primary beams or stimuli. The color may be conveniently specified by giving the amounts required, and this method is called *tristimulus specification*. It is the most fundamental method because the tristimulus specifications of the additive combination of any number of beams is merely the sum of the specifications for each individual beam. If any beam of radiant energy be known by spectrophotometric determination of its spectral components, the tristimulus specification of it may be computed by simple addition. For this purpose we require the tristimulus specifications for each part of the spectrum for the normal observer, and these data expressed in terms of a certain set of primaries as recommended in 1931 by the International Commission on Illumination are almost universally used and are known as the 1931 ICI standard observer and coordinate system for colorimetry.

Recently there has been an effort to supplement the standard coordinate system by expressing the properties of the standard observer in terms of other primaries which yield a spacing of the colors of the same lightness more in accord with that in the constant-lightness planes of the surface-color solid. Such systems, known as uniform-chromaticity-scale systems, have been proposed by Judd, MacAdam, Breckenridge, and Schaub, and by Scofield. The Scofield proposal, made to A.S.T.M. Committee D-1 on Paint, Varnish, Lacquer and Related Products, bears a further resemblance to the constant-lightness

planes of the surface-color solid because it places gray at the origin of the coordinates.

Another method of color specification for objects is by *material color standards*, the color comparison being carried out under identical illuminations for sample and standard by direct visual comparison. Material color standards for special purposes are used in a number of A.S.T.M. specifications such as those of the Union colorimeter for lubricating oils, those of the Saybolt chromometer for refined petroleum oils, and color standards for fastness of textiles to laundering, for fastness of pile floor coverings to light, for soluble nitrocellulose base solutions, for raw soybean oil, for oleo-resinous varnishes, and for organic impurities in sands for concrete.

Transparent color standards of more extended scope include the Lovibond glasses and the Arny solutions.

### Color of Transparent Materials

By Francis Scofield

THE PROBLEM of designating one color out of a family of similar colors has been attacked from a number of angles. The problem can be regarded as selecting a curve through the color three-space, on or near which the colors to be compared lie. The problem is really in two parts. The mechanical and optical problems of holding, illuminating, and viewing the samples and standards will not be considered here. The nature and color characteristics of the standards, however, are very important. The attempts to set up color standards for mineral and vegetable oils, varnishes, resins, and other

Opaque color standards for general purposes include the Munsell system, the Ostwald system, and various color charts preeminent among which is the Maerz and Paul Dictionary of Color. The arrangement of all of these systems of color standards for general purposes bears more or less resemblance to the object-color solid, and in the Munsell system an earnest effort crowned with considerable success was made to have as perfect a resemblance as possible. On this account the ISCC-NBS method of designating the colors of drugs and chemicals was originally worked out in terms of the Munsell system.

It is expected that the detailed description of the various methods of color measurement and specification which is to be given in the papers hereby introduced will assist the various committees of the Society in framing new specifications.

### Hiding Power and Opacity

By R. H. Sawyer

THIN, OPAQUE FILMS such as paint, paper, paper coatings, vitreous enamels, and printing inks are used widely. Such films are usually composed of relatively transparent media opacified by inclusion of finely divided materials of different (usually higher) refractive index. Optical properties of these thin films, such as color, opacity to transmitted light, and hiding power or ability to obscure an underlying contrast, have received much study.

Light falling on a film of transparent medium containing finely divided material of different refractive index is, in part, scattered or reflected at each particle-medium interface. Of the remaining transmitted light, part is absorbed in the particle. Scattering and reflection are functions of refractive index and interfacial area per unit of scattering material (particle size). Opacity, color, reflectivity, and hiding power are, in turn, functions of scattering, reflection and absorption, as well as particle size, particle concentration, and film thickness.

### Color Standards for Opaque Materials

By I. H. Godlove

THE COLOR OF AN OPAQUE object (sample) depends on three sets of factors: (1) the spectral reflectance of the sample; (2) the spectral distribution and the intensity of the incident radiant energy; and (3) the nature (normalcy, etc.) and state of adaptation of the observer's eye. Our control over the last factor consists only in the ability to choose a hypothetical standard representative (and, hopefully, average) observer. Even for him, the color of the sample is still not unique; it depends on the variations of set number 2. Accordingly, standard light

sources have been internationally standardized; of these, one simulates daylight; and we are so familiar with the colors of objects in daylight that the daylight color is to the layman the characteristic color.

The most recently recommended practice considers the luminous reflectance, dominant wavelength, and purity of the light reflected from the sample as the characteristics of the sample object which constitute its color. Thus the color of a sample is taken as its true or apparent capacity to modify the color of the incident light.

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One method of specifying the color (spectrophotometry) measures the inherent capacity of the sample to modify the incident light; and here the standard is ideally a sample producing no modification at all. In practice, this is approached by certain magnesium oxide surfaces.

A second method, which has two or three common variants, finds and specifies a combination of lights which "match" the light reflected from the sample. Such a blend may be: (a) lights from the middle and the two ends of the spectrum (tristimulus or "trichromatic" method), or (b) a fixed light, as average daylight, and a variable light, as successive spectrum lights. In these two variants, the lights are additively combined in varying brightness proportions and compared with the sample.

Another variant (c) belongs primarily under the subject of another speaker. If the lights of the second method be theoretically considered as reflected from the ideal nonmodifying standard, then the third method is the reverse one. In it, the sample color is specified by identifying a material standard which, illuminated by a light of known character, will produce a match. Here again, the standard illuminant commonly simulates average daylight.

The material standards vary from haphazard and variable traditional objects, which lead to unprecise color names such as emerald-green or lemon-yellow, to groups of standards such as the Ostwald and Munsell systems. A "color system" is one which specifies a color by identifying that member of a system of standards which matches the sample. It is usual to consider the systematic character at a maximum when there is much resemblance, as in the Munsell system, of the variations from standard to

standard, to the variations in color perception commonly pictured in the "color solid." The surface-color solid results from analysis and plotting of the three ways in which surface-color perception varies. The variables commonly used for this analysis are hue, saturation, and lightness, although at least two other methods of analysis have been recommended. The ISCC-NBS methods of designating colors is of intermediate character; the names are combinations of simple terms systematically related to the color solid; but each name represents about 30,000 colors normally observable under optimum conditions. Also intermediate are the standards of the "color dictionaries," such as the Maerz and Paul Dictionary of Color and the dyed textile standards of the Textile Color Card Assn. of the U. S. These standards vary in their systematic and fundamental qualities and stress primarily their practical convenience.

Besides these and similar sets of standards, there are many designed for special uses or limited fields of application, for example, standards for the colors of sanitary ware, cast stone, porcelain enamels, school furniture, school busses, aircraft, Army and Navy services, U. S. flag, paints (as in the A.S.T.M. Method of Test for Spectral Apparent Reflectivity of Paint (D 307-39)), pulp and paper, dyestuffs, resins, flowers, corrosion resistance of pigmented films, etc., and for fiber identification. Specification of color may be an analytical index of purity or quality or an aid in control of the color of the final product. The present paper will discuss these various standards in as much detail as the available time permits, stressing primarily their relations to the general phases of color specification as outlined briefly here and their limitations for practical use.

### The Spectrophotometer in the Determination of the Color of Materials

By A. E. Parker

SPECTROPHOTOMETERS are essentially some type of spectrometer together with a photometer; therefore, they are not new instruments. However, the recording spectrometers are new and they have vastly increased the availability of precise measurements in the many fields in which color is involved.

Mention will be made of several types of non-recording instruments and of several recording spectrometers, for

example, Razdek-Mulder, Harrison and Hardy, with special emphasis on the latter.

The various fields of application of this instrument—the testing of paints, papers, etc.—will be discussed from the point of view of research, production, and standardization.

The determination of trichromatic coefficients from spectrophotometric data and their use will be considered.

### Photoelectric Colorimetry

By Richard S. Hunter

THE TERM PHOTOELECTRIC COLORIMETRY is commonly employed to designate both photoelectric tristimulus colorimetry, used to evaluate the appearance of materials, and abridged spectrophotometry, often used to assist in chemical analyses. This paper is devoted to the first type of measurement.

For a photoelectric tristimulus colorimeter, it is desired to find three or four source-filter-photocell combinations of such spectral character that they duplicate the standard ICI observer for colorimetry. With an instrument having these combinations, tristimulus values would be obtained by direct measurement. Although no one has duplicated the ICI observer perfectly, several investigators have obtained source-filter-photocell combinations suitable for the measurement of color differences between spectrally similar samples.

To measure color differences as small as those which the trained inspectors of paints, textiles, plastics, papers, and

ceramic products can see, an instrument must have high precision. If the needed precision is available, a photoelectric tristimulus colorimeter may be used for several purposes; among them are to measure (1) ICI colorimetric values,  $x$ ,  $y$ , and  $\bar{y}$ , relative to those of a spectrally similar calibrated standard, (2) values of  $\alpha$  and  $\beta$ , the chromaticity departures from neutral, in a new uniform-chromaticity-scale mixture diagram for representing surface colors, (3) amounts of color difference between pairs of spectrally similar samples, (4) amounts of color change accompanying fading, (5) whiteness, and (6) yellowness of white and near-white surfaces. Examples of the measurement of these different properties with the author's multi-purpose reflectometer<sup>1</sup> will be cited.

<sup>1</sup> R. S. Hunter, "A Multipurpose Photoelectric Reflectometer," *Journal of Research, Nat. Bureau Standards*, Vol. 25, p. 581 (1940) (*Research Paper 1345*); also *Journal, Optical Soc. America*, Vol. 30, p. 536 (1940).

## Southern California District Meeting on Testing Aircraft Materials

THE MEMBERS OF THE A.S.T.M. Southern California District Committee, centered in Los Angeles, have been considering for some time a meeting of the members in the Southern California District and have decided to sponsor one on Thursday, February 20. The meeting discussion will be based on a paper presented by Dr. W. B. Klemperer, Douglas Aircraft Co., Inc., on the subject "Material Testing Problems Arising from the Advance in Aircraft Performance."

The Society President, W. M. Barr, Union Pacific Railroad Co., is planning to attend this meeting and address the members, and Secretary-Treasurer Warwick will also be present.

Arrangements for the meeting, full details of which will be sent to all members and committee members in the Southern California area, and to members of other engineering groups, are being handled by Mr. John Disario, Metallurgist, Columbia Steel Co., *Chairman* of the District Committee, and E. O. Slater, Vice-President and Manager, Smith-Emery Co., *Secretary*.

## 1941 Photographic Exhibit in June

AMONG THE FEATURES of recent annual meetings of the Society that have attracted growing interest are the photographic exhibits and competitions. The fourth one will be held during the Forty-fourth Annual Meeting in Chicago, June 23 to 27, at The Palmer House.

It will include a section on photomicrography sponsored by Committee E-4 on Metallography.

The exhibits, held annually for the past three years, have included many excellent photographs and have very directly demonstrated what can be done in a quite restricted field, namely, research and testing in the field of engineering materials.

Last year the scope was amplified somewhat to include photographs showing unique applications of materials. A number of photographers submitted prints of this nature. While the group in charge of the 1941 exhibit has not as yet drafted the rules and regulations which will be in effect, undoubtedly they will follow the plan of other years in stressing not the photographic excellence or kind of print, but how well it tells the story. Previously, pictures were rated 70 per cent on this basis.

It is expected that entry blanks will become available in the next few weeks and while copies will be sent to each member and committee member in the Society, those who are particularly desirous of having copies as soon as the blanks become available can write A.S.T.M. Headquarters and their names will be placed on a special list.

The responsibility for the Fourth Photographic Exhibit and Competition has been assigned to a committee headed by A. W. Laird, Metallurgical Engineer, Western Electric Co., Inc. This committee now in course of organization will develop the theme, general rules, and take care of the various details involved, including judging and the like. Committee E-4 will be represented on this committee, to tie in closely the general section and that on photomicrography.

## Cleveland District to Discuss "Specifications—Their Extreme Importance in the Present Emergency"

WHAT PROMISES TO be a most interesting meeting on the subject "Specifications—Their Extreme Importance in the Present Emergency" is being arranged by the A.S.T.M. Cleveland District Committee to be held at the Allerton Hotel, E. Thirteenth St. and Chester Ave., Cleveland, on Thursday evening, January 30. Arrangements for the meeting are being carried out by Arthur J. Tuscany, Managing Partner, Tuscany, Turner and Associates, *Chairman* of the District Committee. J. H. Herron, President, The James H. Herron Co., is *Past-chairman* of the group, and Col. W. W. Rose, Executive Vice-President, Gray Iron Founders' Society, Inc., is *Secretary*.

Preceding the technical session will be an informal dinner to begin promptly at 6:15 o'clock (assembly at 6:00). Ray T. Bayless, Assistant Secretary and Editor, American Society for Metals, is in charge of the dinner and reservations with the accompanying remittance should be sent direct to him. The dinner charge is \$1.35.

A notice has been mailed to all members in the Cleveland district and Mr. Tuscany has arranged to give wide publicity to the meeting through the Cleveland sections of the various national associations and other Cleveland groups including the Engineers' Club. All of the members of these organizations are cordially invited to attend the dinner and meeting.

### TECHNICAL SESSION

The discussion at the meeting will be divided into three parts. The presiding technical chairman will be Mr. Herron who will introduce three co-chairmen to act jointly with him as the three topics selected come up for discussion. The specific subjects to be covered and the co-chairmen who will respectively be in charge of the programs, are as follows:

CAST METALS—F. G. Steinebach, Editor, *The Foundry*, Cleveland  
PIPE AND TUBING—H. R. Redington, *Secretary*, Specification Committee,  
National Tube Co., Pittsburgh

GENERAL IRON AND STEEL PRODUCTS—L. B. Grindlay, Republic Steel Corp., Cleveland

A number of technical authorities will assist each co-chairman in presenting prepared talks and discussion, and following the last topic, the meeting will be thrown open for general discussion, with comments welcomed from the floor. Since the proceedings of the meeting will not be recorded or published, a frank discussion is anticipated.

A number of engineers and technologists connected with various branches of the Government, Ordnance Department, Army and Navy, and U. S. Engineers Office, are being invited to participate in the meeting.

Each of the topics chosen is of much importance in the Cleveland district, and even though the subjects selected may not be of specific concern to some of the members and others in the group, the discussion is bound to be of broad interest and applicable in many aspects to all types of materials.

# The Instituto Argentino de Racionalización de Materiales— IRAM

## The Argentine Institute of Standardization of Materials

THIS ARTICLE was prepared for the BULLETIN by Ing. Marcelino A. Ceriale, Director General of IRAM (Instituto Argentino de Racionalización de Materiales) to whose vision, organizing ability, and energetic efforts its existence and development have been largely due.

Ing. Ceriale is a graduate in mechanical and electrical engineering of the National University of La Plata, and after being connected with several electric power enterprises, entered the service of the Argentine State Railways of which he became Chief Inspector of Materials and Specifications, directing the studies of Standardization for the Railway Administration.

His experience in this work led him to study the possibility of extending the benefits of standardization of materials to all national departments, and in May, 1935, IRAM was founded with Mr. Ceriale as its

President. Under his administration the Institute's work became of great importance and of international aspect.

The activities of Mr. Ceriale and the Institute have become well known in technical, economic, and university circles by his writings and lectures and the discussions which took place at the First South American Engineering Congress in Santiago, Chile, in 1939 stimulated interest in standardization in many of the countries of South America.

The Argentine Government gave official recognition to IRAM's work by creating in 1937 the National Standardizing Commission (Comisión Nacional de Uniformación de Materiales) of which Ing. Ceriale was named General Secretary, and at IRAM's annual meeting in April, 1940, Mr. Ceriale was unanimously voted the title of "Creator of IRAM."

### WHAT IRAM Is

THE INSTITUTO ARGENTINO de Racionalización de Materiales—IRAM (Argentine Institute of Standardization of Materials) is a civil entity, with legal status, organized in the Argentine Republic with the object of establishing standards for materials, their applications, and uses. Its membership comprises official and private entities and personal members interested in this work.

Among the outstanding stipulations of IRAM's statutes the following are worthy of comment:

1. Its members are grouped in three divisions representing, respectively, (a) scientific or general interest, (b) industry, and (c) consumers.

2. One of its objects is to work for improvement and coordination of existing laboratories and the creation of new laboratories for studying and investigating materials.

3. The "Directing Council" is composed of 18 members with six alternate members, six and two, respectively, corresponding to each of the three membership divisions mentioned.

4. In the procedure to be followed for the adoption of standards it is established that the respective committees must be made up of representatives of the divisions *a*, *b*, and *c*, in such a way as to give *an even balance between the representation of consumers and producers*.

5. All Standards are first approved provisionally and remain as provisional during a long trial period. They are given publicity in the official organ *Informaciones—IRAM* and any observations made are carefully considered by the Institute.

### HOW AN IRAM STANDARD IS PREPARED

The accompanying chart shows the normal course of a "Standard" from the time it is first proposed until it finally becomes an "Official IRAM Standard." In addition, the chart may be supplemented by the following observations:

The first step in the consideration of a Standard consists of the preparation of a "summary of antecedents" (planilla de antecedentes) in which a résumé is given of corresponding standards of other countries, studies which have already been made of the subject in Argentina, existing official specifications, publications applying to the subject, a glossary of pertinent technical terms, special notation that may apply, etc. With this in mind IRAM maintains a library containing an up-to-date set of the standards published by the most important countries, this being the most complete collection of standards in the Argentine Republic and probably in South America.

This "summary of antecedents" passes then to a specialized subcommittee which studies the matter and prepares a draft of the proposed standard which is then referred to the respective committee which has been named to handle this standard. This committee discusses and modifies the draft if it considers this advisable and this draft is then referred to the Committee on Nomenclature, Symbols and Coordination whose duty it is to assure that the standard complies with IRAM's general requirements as laid down in its "Standard for Standards."

Subsequently the project is referred to the General Standards Committee which brings together and checks the work of all of the various committees that have intervened in the preparation of the standard and then passes the finished "Projected Standard" on to the Directing Council of the Institute. The Council considers it and if approved issues it as a "Proposed IRAM Standard" under which form it is transmitted to the National Commission



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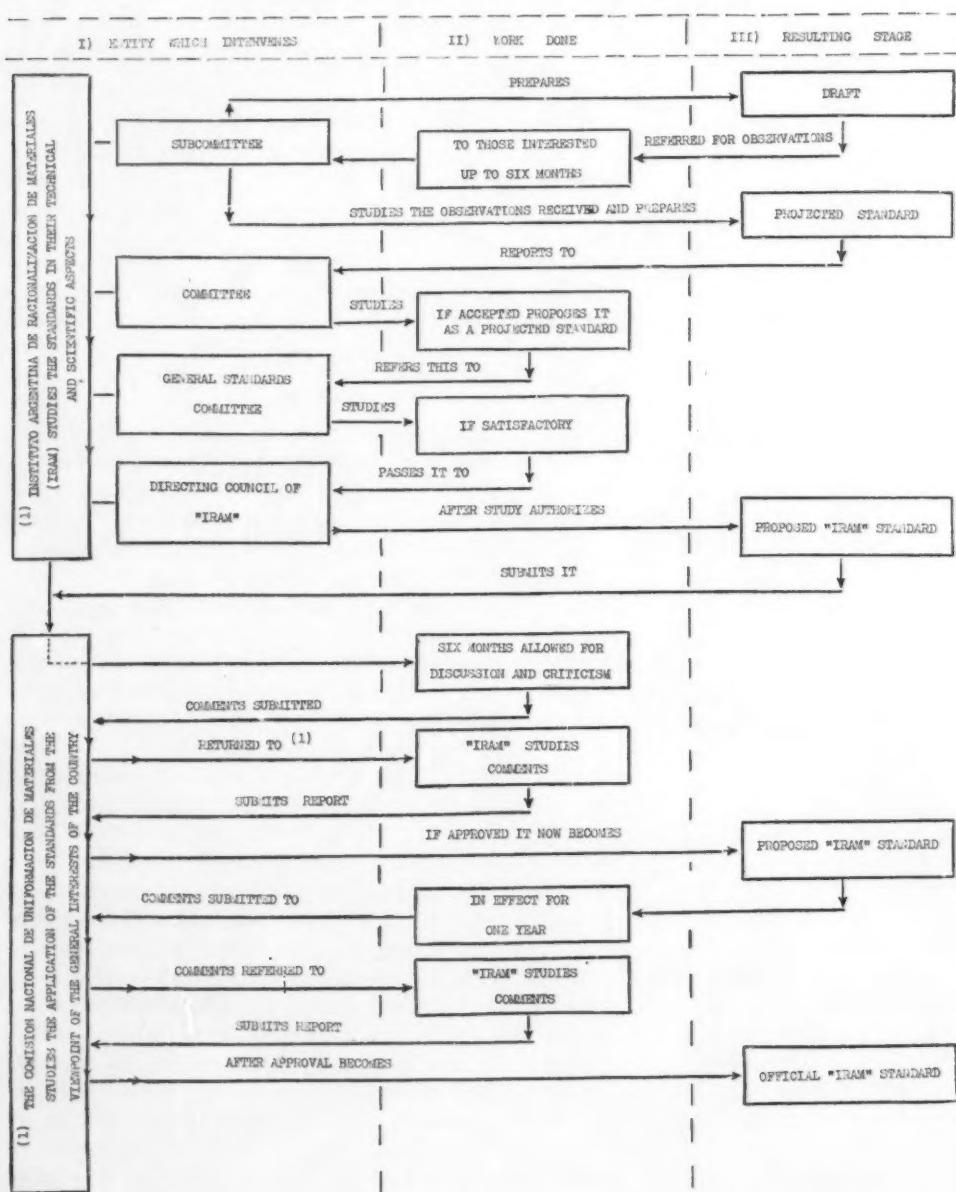
for Standardizing Materials, the governmental agency which finally gives official status to IRAM's work.

Briefly then the successive steps through which a Standard passes are: Preliminary Plan; Draft; Projected Standard; Proposed IRAM Standard; Official IRAM Standard.

#### WORK DONE BY IRAM

Up to the present some fifty standards-committees and subcommittees have been formed involving participation by some 500 technicians, principally graduate engineers, chemists, and architects, who have spontaneously given their collaboration to the study and preparation of IRAM standards. Twenty-five standards have already been approved, 22 of these have been published and 95 additional standards are now under study.

#### INSTITUTO ARGENTINO DE RACIONALIZACION DE MATERIALES Steps in the Preparation of "IRAM" Standards



(1) THE COMISION NACIONAL REFERS TO "IRAM" THOSE COMMENTS WHICH IT IS CONSIDERED SHOULD BE STUDIED FROM THE TECHNICAL AND SCIENTIFIC STANDPOINT.

#### POSITION OF IRAM IN ARGENTINA

Recognizing the advantages accruing from the standardization of materials, the National Government by a decree of December 14, 1937, created the National Standardizing Commission (Comision Nacional de Uniformacion de Materiales) with the object of giving official approval to IRAM standards and seeing that they are followed. The Ministries and principal Government Departments, the universities, and also certain private entities especially authorized by the Government are represented on the National Commission. Its relation with IRAM is set forth in Article 4 of the decree as follows:

"The National Standardizing Commission will make use of the Argentine Standardizing Institute—IRAM—as the centralizing body for technical and scientific studies of standards in order to maintain uniformity of methods and ideas."

"Any other entity now existing or which may be formed in the future for the study of standardization must refer any standards which they may draw up to the National Standardization Commission which will, after a due study and report has been made by IRAM, put them into effect if considered advisable."

This gives official ratification to IRAM's work with a corresponding increase in influence and results. Argentina thus has in IRAM a technical organization for preparing its standards and in the National Commission an official body whose duty it is to see that IRAM's technical work does not affect adversely the country's national and international interests. As a result an IRAM standard not only takes into account technical and scientific considerations, but also those of public interest, and this should enable Argentina to issue the best possible standards.

# Studies of the Measurement of Specific Surface by Air Permeability

By R. L. Blaine<sup>1</sup>

MUCH WORK HAS been done on the permeability of granular materials based on the assumption that the interstices formed by closely packed granules are analogous to a group of capillaries in their behavior to flow of fluids through a bed of material. D'Arcy's empirical equation for permeability was based on measurements of the flow of water through sands and sandstones. Kozeny later derived an equation for permeability by assuming that the bed is equivalent to a group of parallel similar channels. Later Carman (1, 2, 3)<sup>2</sup> verified Kozeny's work and arrived at an equation relating specific surface to permeability. Carman used liquids as the permeating fluid, which was satisfactory for coarser particles but caused difficulties with very fine materials due to the effect of the adsorbed liquid layers decreasing the effective cross-section of the capillary channels. Lea and Nurse (4) suggested the use of gas as the fluid in making permeability measurements and described an apparatus and a series of experiments. The results of these investigations appeared so promising that the further study reported in this paper was carried out. Experiments were made to determine the reproducibility of results obtained on portland cement by different operators and the applicability of the apparatus to other materials, and to compare the relative specific-surface values obtained by the air-permeability method described by Lea and Nurse with those obtained by the commonly used Wagner turbidimeter method.

## THEORY OF AIR PERMEABILITY METHOD

The equation arrived at by Carman showing the relationship of specific surface to permeability is as follows:

$$S_o = \sqrt{\frac{g}{kK\nu} \cdot \frac{\epsilon^3}{(1-\epsilon)^2}} = 14 \sqrt{\frac{1}{K\nu} \cdot \frac{\epsilon^3}{(1-\epsilon)^2}} \dots (1)$$

where  $S_o$  = surface per unit volume of particles in square centimeters per cubic centimeter;

$g$  = acceleration due to gravity, 980 cm. per sec. per sec.;

$\epsilon$  = porosity, that is, volume of pore space per unit volume of bed =

$$1 - \left[ \frac{\text{wt. of material in grams}}{\text{density in grams per cubic centimeter}} \right] \text{volume of the bed in cubic centimeters}$$

$k$  = a constant which was found to have a value of 5;

$K$  = permeability, that is, apparent linear rate of flow of fluid in centimeters per second for unit hydraulic gradient; and

NOTE.—DISCUSSION OF THIS PAPER IS INVITED, either for publication or for the attention of the author. Address all communications to A.S.T.M. Headquarters, 260 S. Broad St., Philadelphia, Pa.

<sup>1</sup> Assistant Materials Engineer, National Bureau of Standards, Washington, D. C.

<sup>2</sup> The italic numbers in parentheses refer to the reports and papers appearing in the list of references appended to this paper.

$\nu$  = kinematic viscosity in square centimeters per second.

Later Lea and Nurse expressed  $1/K\nu$  of this equation in terms of apparatus constants and manometer readings made with an air-permeability apparatus of the capillary-flow-meter type, making use of the relations:

$$K = Q/A_i$$

$Q = C b_2 \rho_4 / \eta$ , a form of the Poiseuille equation

$$i = b_1 \rho_3 / \rho_2 L$$

$$\nu = \eta / \rho_2$$

$$\rho_3 = \rho_4$$

They furthermore expressed the specific surface as the surface area per gram of material, according to the relation:

$$S_w = \frac{S_o}{\rho_1} = \frac{14}{\rho_1(1-\epsilon)} \sqrt{\frac{\epsilon^3 A b_1}{C L b_2}} \text{ or } \frac{14}{\rho_1} \left( \frac{\epsilon^3}{(1-\epsilon)^2} \cdot \frac{A b_1}{L C b_2} \right)^{1/2} \dots (2)$$

where  $S_w$  = specific surface in square centimeters per gram;

$\rho_1$  = density of material tested;

$\rho_2$  = density of air used as permeating fluid;

$\rho_3$  = density of fluid in manometer measuring pressure difference across bed of material;

$\rho_4$  = density of fluid in manometer measuring pressure difference across capillary;

$Q$  = rate of air flow in cubic centimeters per second through the capillary;

$i$  = hydraulic gradient, that is, the ratio of the head of the permeating fluid to the thickness of the bed;

$C$  = a constant for the flowmeter;

$A$  = cross-sectional area of bed of material in square centimeters;

$L$  = depth of bed in centimeters;

$b_1$  = difference in level of liquid in manometer measuring pressure difference across the bed of material in centimeters;

$b_2$  = difference in level of liquid in manometer measuring pressure difference across the capillary in centimeters; and

$\eta$  = viscosity of air in poises.

This equation was used in calculating the results obtained in the tests here reported.

## DESCRIPTION AND OPERATION OF APPARATUS

The air-permeability apparatus (Fig. 1) with which the tests were made was similar to that used by Lea and Nurse. The permeability cell,  $A$ , was made of 1-in. (outside diameter) brass tubing and had an inside diameter of 2.38 cm. as compared to 2.54 cm. for the Lea and Nurse cell. The filter disk (Norton porous filter RA 225) sealed between the upper and lower parts of the cell with Duco cement

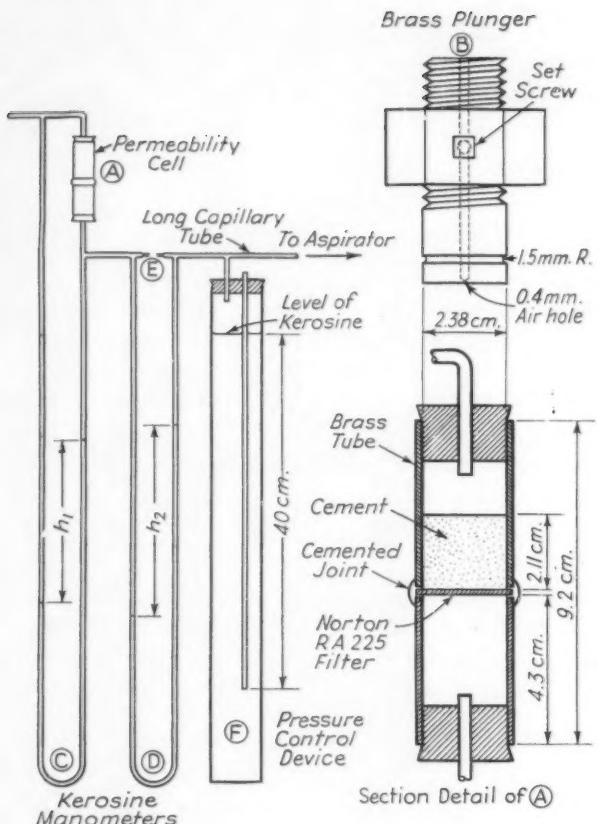


Fig. 1.—Air-Permeability Apparatus.

was used in place of a perforated metal disk and filter paper. The outside edge of the filter disk was also sealed to insure against leakage. The plunger, *B*, used to compact the powder in the cell to a definite volume had an adjustable collar with a set screw. The plunger was made to fit snugly the inside of the permeability cell. The manometers, *C* and *D*, 50 cm. long and half filled with kerosine were used to measure the pressure drop across the bed of cement and that across the capillary, respectively. The capillary tube, *E*, was made of four 3-ft. lengths of capillary tubing having an average internal diameter of 0.675 mm. This average diameter was calculated from the weight and length of a column of mercury in the capillary. The value reported is the average for each of the capillary tubes. The several lengths were connected in series with rubber tubing and sealed with a rosin-paraffin mixture. The capillary was calibrated against a flow meter at pressures of from 4 to 27 cm. of kerosine. The equation constant, *C*, of the apparatus was  $1.252 \times 10^{-6}$  as compared to  $3.47 \times 10^{-6}$  for the capillary used by Lea and Nurse. A constant pressure difference was obtained by use of a water aspirator and a kerosine release valve, *F*. All connections were made with tight-fitting heavy rubber tubing. The seals were further insured by coating the joints with a rosin-paraffin mixture.

An appropriate weight of powder<sup>3</sup> was placed in the permeability cell and leveled by gently tapping the sides. The powder was then slowly compressed by means of the plunger until the plunger collar was in contact with the

<sup>3</sup> The volume of the bed of material was kept constant at 9.39 ml., while the amount of powder used was varied, depending on the specific gravity of the material and the porosity desired.

top of the cell. While pressure was maintained on the plunger it was rotated one complete revolution and then withdrawn slowly with a rotary motion. Any powder adhering to the sides of the plunger or any which had been forced into the plunger vent was returned to the cell and the bed of powder again compressed as previously and the plunger withdrawn slowly. The cell was then connected to the apparatus and the pressure difference applied. Manometer readings were taken 5 min. after air flow was started.

Calculations of specific surface were made with the use of the same assumptions and the formula proposed by Lea and Nurse.

Determinations of the resistance of the filter alone were made after every four determinations of fineness. The filter disk was cleaned with HCl after each 20 determinations, or more often if the condition of the filter disk required it. Its resistance was of the order of 1 per cent of the resistance of the capillary; hence corrections were not made on the results here reported.

## TESTS

### Studies of Testing Operation:

Studies were made of the testing procedure to find some of the limitations and precautions which must be observed.

Other investigators have shown that the relation in Eqs. 1 and 2 between the porosity function,  $\epsilon^3/(1 - \epsilon)^2$ , the permeability, and specific-surface values hold reasonably well for some finely divided materials. Some additional data are presented in Table I showing the effect of

TABLE I.—SPECIFIC SURFACES OF RAW MIXES, HYDRATED LIMES, AND PORTLAND CEMENT, COMPAKTED TO VARIOUS DEGREES.

Material	Porosity, $\epsilon$	Number of Determinations	Specific Surface, sq. cm. per g.	Mean Variation of Values Obtained at Different Porosities, per cent
Raw mix No. 1	0.442	1	5330	1.2
	0.461	1	5120	
	0.482	5	5160 $\pm 0.6\%$	
	0.502	1	5160	
	0.522	1	5100	
Raw mix No. 2	0.461	1	Avg. 5170	0.8
	0.482	5	5000	
	0.502	1	5160 $\pm 0.5\%$	
	0.522	1	5110	
	0.541	1	5150	
Raw mix No. 3	0.451	1	Avg. 5100	1.6
	0.470	1	4890	
	0.490	5	4920	
	0.509	1	4860 $\pm 0.2\%$	
	0.528	1	4800	
Cement A (See Table II)	0.549	1	4730	0.6
	0.459	1	4680	
	0.476	1	Avg. 4810	
	0.493	5	3770	
	0.510	1	3810	
Hydrated Lime No. 1	0.527	1	3750	10.4 3.6 <sup>a</sup>
	0.544	1	3710	
	0.617	1	Avg. 3750	
	0.638	1	16230	
	0.660	1	15550	
Hydrated Lime No. 2	0.680	5	15500	10.4 3.6 <sup>a</sup>
	0.702	1	14950 $\pm 0.6\%$	
	0.723	1	14300	
			10060	
			Avg. 14430	
Hydrated Lime No. 3			Avg. 15310 <sup>a</sup>	
	0.680	3	10700	
	0.680	1	17400	
Hydrated Lime No. 4	0.680	1	21300	

<sup>a</sup> If last value of series is disregarded.

TABLE II.—REPRODUCIBILITY OF SPECIFIC SURFACE VALUES OF FOUR CEMENTS.

Operator	Specific Surface, sq. cm. per g. <sup>a</sup>	Operator's Variation from His Average, per cent	Specific Surface, sq. cm. per g. <sup>a</sup>	Operator's Variation from His Average, per cent	Specific Surface, sq. cm. per g. <sup>a</sup>	Operator's Variation from His Average, per cent	Specific Surface, sq. cm. per g. <sup>a</sup>	Operator's Variation from His Average, per cent	Average Variation of the Different Operators, per cent
A	3750	0.4	2480	0.3	2980	0.7	5200	1.2	0.65
B	3760	0.6	2480	1.7	3000	1.0	5150	2.4	1.40
C	3710	1.1	2470	0.5	2960	0.7	5160	1.9	1.05
D	3690	1.0	2490	1.2	2920	1.6	5130	2.4	1.55
E	3720	0.9	2490	0.2	2980	0.9	5050	1.4	0.85
F	3680	0.9	2490	0.4	2960	0.6	5130	0.6	0.60
G	3720	0.3	2500	0.5	3000	1.4	5060	1.2	0.90
H	3770	1.3	2530	0.4	3020	0.7	5150	3.0	1.10
Average Variation of averages	3720	0.8	2490	0.65	2980	0.95	5130	1.76	
Percentage variation of 40 determinations		0.8		0.44		0.80		0.80	
		0.97		0.80		1.11		2.19	

<sup>a</sup> Average of five determinations by each operator.

varying the porosity on the specific-surface values of a few materials. The change in specific-surface values with change in porosity is very small for the portland cement and the raw mixes, although there is some indication of a slight decrease in specific surface with increasing porosity. This trend is quite evident, however, for hydrated lime, indicating differences in the structure of the bed of material such as agglomeration or channeling of particles and bridging causing low fineness values to be obtained when the powder is not compacted to a uniform and low porosity. It is evident from Table I, however, that this effect is not very great except when the porosity is very high.

If the bed of material is excessively compacted, it has a tendency to spring back to a slightly greater volume than is indicated by the plunger collar. If, on the other hand, the bed is very lightly compacted, a slight jar may cause settling, or loosening of the bed from the cell wall. Either eventuality will lead to erroneous results. Compressing the bed firmly tends to minimize the anomalous behavior.

Lea and Nurse compacted the cement to a porosity of 0.492 in testing portland cement. This was found to be satisfactory for all except very finely ground high-early-strength cements which were difficult to compact. When making tests on lime or mixtures of lime and cement it was found necessary to use greater porosities.

Care must be exercised in compressing the bed to the same accurately determined depth in every test. For example, an error of 0.1 mm. in 21 mm. in measuring the height of the bed of material frequently causes an error of more than 1 per cent in the computed porosity. The plunger must be inserted very slowly or a considerable quantity of powder will be pumped into the plunger vent or will go up around the edges. The plunger must also be withdrawn slowly or the rush of air through the vent will cause a pocket to be formed in the bed of material.

Lea and Nurse took a number of manometer readings at different levels (that is, for different rates of air flow) and used the average  $b_1/b_2$  ratio. It was noted that at any pressure difference the  $b_1/b_2$  ratio changed considerably during the first few minutes. The time required for the manometers to reach equilibrium depends on the fineness and porosity of the material, the rate of air flow, and size of capillary. It was noted in some preliminary work at this laboratory that with different rates of air flow, the  $b_1/b_2$  ratio was slightly different with the same bed of material. This was found with two different capillaries. Lea and Nurse used a rate of air flow of from 1 to 4 liters per hour. The test results reported in this paper were obtained with air flows of about  $1/2$  liter per hour.

The porous filter was used instead of the perforated plate and filter paper of the Lea and Nurse apparatus because it could be better sealed into the permeability cell. Difficulties with leaks were encountered when filter paper was used, due principally to the design of the permeability cell. One disadvantage of the porous filter was that the resistance changed with use, because of clogging of the pores which necessitated cleaning with acid. Results obtained in later tests with a properly designed permeability cell indicate that the perforated disk and filter paper are satisfactory.

#### REPRODUCIBILITY OF TEST RESULTS WITH PORTLAND CEMENTS

Experiments to determine the reproducibility of specific-surface values obtained with the air-permeability apparatus were made on four cements of different degrees of fineness. Eight operators each made five fineness determinations on each of the four cements. The results are presented in Table II. The only experience seven of the operators had had with the air-permeability apparatus was a group demonstration and two practice determinations each. In the practice determinations the average variation for all tests was  $\pm 1.1$  per cent from the grand average. These trials indicated that the reproducibility is as good as, or better than, that obtained with the Wagner turbidimeter. The reproducibility of results by various operators with little training indicates the simplicity of the test method.

#### ADAPTABILITY OF THE AIR-PERMEABILITY APPARATUS TO MIXTURES AND OTHER MATERIALS

Various proportions of a hydrated lime and a portland cement were mixed to ascertain the suitability of using the air permeability apparatus with such mixtures. The specific surface was determined on both the hydrated lime and the portland cement by means of the air-permeability apparatus and from these values the specific surfaces of the various mixtures were calculated. The porosity of each mixture was adjusted to give approximately the same rate of flow of air through the bed in each case. The average difference of the experimental from the calculated specific surface value was 0.6 per cent (see Table III).

The specific surfaces were determined on three raw mixes of dry-ground cement (Table I). In the 5 determinations on each sample made at an appropriate porosity, the values of specific surface were 5160, 5160, and 4860 sq. cm. per g. with percentage mean variations of the individual from

TABLE III.—SPECIFIC SURFACE OF MIXTURES OF HYDRATED LIME AND PORTLAND CEMENT.

Material	Parts by Weight Hydrated Lime	Cement	Porosity, %	Number of Determinations	Specific Surface, sq. cm. per g.		Difference between Observed and Calculated Values, per cent
					Determined	Calculated	
	100	0	0.680	5	14.950 ( $\pm 0.6$ ) <sup>a</sup>		
	80	20	0.656	5	12.850 ( $\pm 0.5$ ) <sup>a</sup>	12.705	1.1
	60	40	0.634	5	10.540 ( $\pm 0.5$ ) <sup>a</sup>	10.460	0.8
	40	60	0.593	5	8.260 ( $\pm 0.5$ ) <sup>a</sup>	8.215	0.5
	20	80	0.541	5	5.970 ( $\pm 0.7$ ) <sup>a</sup>	5.970	0.0
	0	100	0.492	40	3.720 ( $\pm 0.8$ ) <sup>b</sup>	...	...

<sup>a</sup> Percentage variation from average of five determinations.<sup>b</sup> Percentage variation of 40 determinations by eight operators.c Specific surface of mixture = (per cent lime  $\times$  specific surface of lime + per cent cement  $\times$  specific surface of cement)  $\div$  100.

the average of each group of  $\pm 0.6$ ,  $\pm 0.5$ , and  $\pm 0.2$ , respectively.

In order to test the adaptability of the air-permeability apparatus to other materials, three determinations were made on each of four samples of whiting and four samples of hydrated lime (Table I). One sample of whiting, which was a calcite, had a specific surface value of 6250 sq. cm. per g. Two samples of ground limestone whiting had specific-surface values of 9000 and 15,750 sq. cm. per g., respectively, and a precipitated calcium carbonate had a value of 22,500 sq. cm. per g.

#### RELATIVE SPECIFIC-SURFACE VALUES OBTAINED BY AIR PERMEABILITY AND OTHER METHODS

Lea and Nurse reported values of specific surface as obtained with the air-permeability apparatus of from 1.6 to 1.8 times the values obtained with the Wagner turbidimeter (5). In the present investigation the ratios obtained with portland cement (see Table IV) varied from 1.77 to 1.92. The raw mixes and the flint showed slightly lower ratio of air permeability to turbidimeter values.

One of the samples of hydrated lime had a specific surface of 10,700 sq. cm. per g. by the air-permeability method. This sample of lime had a specific surface of 12,000 sq. cm. per g. when tested by means of a sedimentation apparatus used by Bishop (6 and 7).

#### DISCUSSION

In any test method, simplicity and reproducibility of test results are desired. The air-permeability apparatus is simple to operate and there is little likelihood of a failure of any of its parts other than by breakage. The results of duplicate tests by one operator or by a number of operators show good reproducibility. The time required for making a test is short (approximately 8 to 10 min.) and the apparatus is, therefore, suitable for plant control work.

On the other hand, it was noted that slight differences of specific-surface values were obtained by varying the rate

of air flow through the same bed. Testing very fine materials such as hydrated lime at various porosities indicated that there is probably an agglomeration or a channeling of particles tending to result in low specific-surface values with high porosity. However, at any one porosity and rate of flow of air, the results were reproducible.

If the apparatus is to be used for specification purposes, it may be necessary to specify for any given material the rate of air flow through the bed as well as the area, depth, and porosity of the bed.

Although the specific-surface values obtained by the air-permeability method are at variance with the results obtained by the use of the turbidimeter, the two methods are based on different primary assumptions and each method is essentially a comparative one. Certain behavior characteristics of portland cement seem to indicate that the values of specific surface obtained with the air-permeability method are closer approximations of the true values than are obtained with the turbidimeter. However, the determination of absolute values of surface areas of irregularly shaped granules will require further study.

#### CONCLUSIONS

The Lea and Nurse air-permeability apparatus affords a ready means of comparing the specific surfaces of powdered materials. The procedure is fast and simple and the test results are reproducible. The air-permeability apparatus is well adapted to test materials in the range of fineness of portland cement, and can also be used for testing finer materials. The air-permeability apparatus can be used to determine the specific surfaces of mixtures of two or more components having different specific gravities.

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TABLE IV.—COMPARISON OF SPECIFIC SURFACE DETERMINED BY TWO METHODS.

Material	Specific Surface, sq. cm. per g.		Ratio of Specific Surfaces, Permeability Apparatus Turbidimeter
	Air-Perme- ability Apparatus	Wagner Turbidi- meter	
Cement A	3720	1940	1.92
B	2490	1320	1.89
C	2980	1650	1.81
D	5130	2890	1.77
White portland cement	3120	1620	1.92
Raw mix No. 1	5160	2960	1.74
No. 2	5160	2980	1.73
No. 3	4860	2850	1.70
Potters flint	4710	3100	1.52

# Symposium on Tools of Analytical Chemistry

THE FOLLOWING abstracts cover papers presented in the Symposium on Tools of Analytical Chemistry held during the Forty-third Annual Meeting of the Society in Atlantic City, June 25 and 26, 1940. In this symposium, the Society acted as host to the analytical members of the Physical and Inorganic Chemistry Division of the American Chemical Society, for the purpose of presenting recent developments in chemical analysis, and of providing an opportunity to discuss common problems.

Two formal sessions were held. The first dealt with microanalysis, polarography, chromatography, internal electrolysis, radioactive indicators, electronic circuits applied to analytical chemical procedures, and the theory and practice of pH determinations and control using the glass electrode. The second session covered micro-gas

analysis methods and their application to research, new and forgotten aspects of compounds in inorganic analysis and recent developments in cerate oxidimetry. These sessions were followed by two enjoyable and instructive sessions covering spectrographic analysis, and a tie-in session dealing with motion pictures of spectrochemical and microanalytical installations in industry.

All sessions were outstanding in the caliber of the speakers and the excellence of their papers, in the large attendance and sustained interest, and in the formal and informal discussions of problems attending the chemical and spectrochemical testing of materials.

G. E. F. Lundell  
Co-chairman, Symposium Committee

## Some Newer Trends in Analytical Chemistry

By Beverly L. Clarke<sup>1</sup>

ANALYTICAL chemists are often irritated by a proneness exhibited by their colleagues in other branches of chemistry to regard the analyst as one of the lower forms of chemical life. This irritation is altogether justified, not only because analysis has made great and essential contributions to all branches of chemistry, but also because the scoffing non-analyst himself spends probably the major portion of his time in the laboratory carrying out chemical analysis, even though he gives these operations other names.

The chemist has but three primary kinds of activity, no matter what his special branch of the science: analysis, synthesis, and sensory perception. He tears molecules or atoms apart, he puts them together, and with his senses, or artificial extensions thereof, he sees, smells, hears, or feels what happens. When the Curies extracted radium from pitchblende, they were carrying out a chemical analysis of that ore for one of its constituents. True they were not able to turn to an A.S.T.M. Book of Standards for their method for this analysis. True the analysis proved to be one of infinite difficulty and complexity. But it was analysis nevertheless, and similar in kind if not in degree to the methods that have been used since the time of Berzelius for mineral analysis. Again, Dalton's atomic hypothesis would have been accorded but scant credence had he not been able to obtain supporting data through the methods of quantitative analysis. Even the synthetic organic chemist has to analyze his natural compound before he can systematically begin its synthesis.

There is of course a practical distinction between the work of the analytical chemist and that of chemists like the Curies. It lies in the objective of the tearing down process. It was desired to extract radium from pitchblende, not primarily to find out whether it was there

(qualitative analysis) or how much was there (quantitative analysis), but because the Curies wanted some radium to study. Other researchers have other reasons for carrying out analytical processes, but custom has designated as analytical chemists those whose immediate interest is the discovery of the composition, qualitative or quantitative, of substances. Thoughtful analytical chemists contend that this is a perfectly respectable objective.

The analytical chemist is finished with his job when he can write down the percentage composition of his sample. With other chemical workers this is frequently the beginning; the essence of the research seems to lie in discovering the explanation of why the chemical composition is as it is. But it is an indisputable fact that the analysis of a substance for the limited purpose of determining its composition can be and frequently is an operation requiring skill, experience, ingenuity, and chemical common sense of a very high order indeed.

Despite the importance of chemical analysis it remained until comparatively recent years a neglected branch of the science.<sup>2</sup> One cannot set any date in the history of chemistry as the beginning of analysis; as far back as we care to go it appears that chemists were interested in what things were made of. Robert Boyle is credited with having originated the term "chemical analysis," and other outstanding names as we pass up into the Nineteenth Century are Lavosier, Berzelius, and Stas. During the first quarter of that century analytical chemistry was in flower; this was so because it absorbed the interest of many of the best minds among chemists. But, when in 1828 Wöhler synthesized urea and initiated the Age of Synthesis, analysis was rapidly relegated to the background. Later on, around 1880, interest picked up again in analy-

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<sup>2</sup> The author has treated this point in some detail elsewhere: *Journal of Chemical Education*, Vol. 14, p. 561 (1937); *Bell System Technical Journal*, Vol. XV, p. 483 (1936).

sis, but once more a usurper arose in the form of the new branch called physical chemistry, and analysis lost out again.

At this period quantitative chemical analysis fell into two broad divisions, gravimetric and volumetric, with respect to the methods used for the measurement of quantity of the pure compound of known composition containing the element to be determined. Many of the methods used were extremely circuituous and tedious. For the most part, no special search had been made for reactions peculiarly suited to analytical processes, and few pieces of apparatus deliberately designed for analysis were available. Through the last decades of the Nineteenth Century, the development by physical chemists of an understanding of the nature of solution gave the analysts an insight into the mechanisms of many of their reactions and enabled them to effect improvements. This also brought into prominence a hitherto little used type of reaction for producing a pure substance for measurement—electroanalysis.

The classical period of analytical chemistry may be said to have ended approximately at the beginning of the present century. With the development of physical chemistry it became possible to measure the quantity of the pure compounds obtained as end products in analytical processes, through their physicochemical properties as well as through direct measurements of weight and volume. Examples of such properties are density, color, refractive index, emission spectra, vapor pressure, and electrode potentials. Thus, with the entrance of analytical chemistry into its modern phase, it became necessary to add to

the two previously mentioned divisions as to method of measurement, volumetric and gravimetric, a third division—physicochemical methods.

It is this third division that the writer has in mind in using the phrase, "newer trends in analytical chemistry." It is not the intention to make this paper definitive, in the sense of completely discussing all the newer trends. This would be not only impossible but undesirable, since other papers in this symposium treat a number of the topics falling under this head.

Undoubtedly the most important of the newer trends is microanalysis. As originally conceived by its founders, microanalysis was not so much an adaptation of physicochemical measurement methods as a declaration of independence from classical tradition. The Austrian chemists, Emich and Pregl, in the several years centering around 1910, made, in effect, the simple declaration that henceforth analysts were not to consider themselves bound to use exclusively either the apparatus, the techniques, or the reactions devised by the synthesists for their own ends. The most obvious limitation imposed on the analyst by this classicism was in the scale of operations. There are obvious disadvantages in attempting to manipulate drops of solutions in 6-in. test tubes, or in trying to weigh microgram samples on balances built for milligrams. Pregl and Emich asked themselves the question: Is there any good reason why the analyst may not design his own apparatus so that it is suitable, in size and shape, to the work he plans to do with it? Finding no good reason, and being immediately interested in analyzing very small samples, they made replicas in miniature of standard laboratory ap-

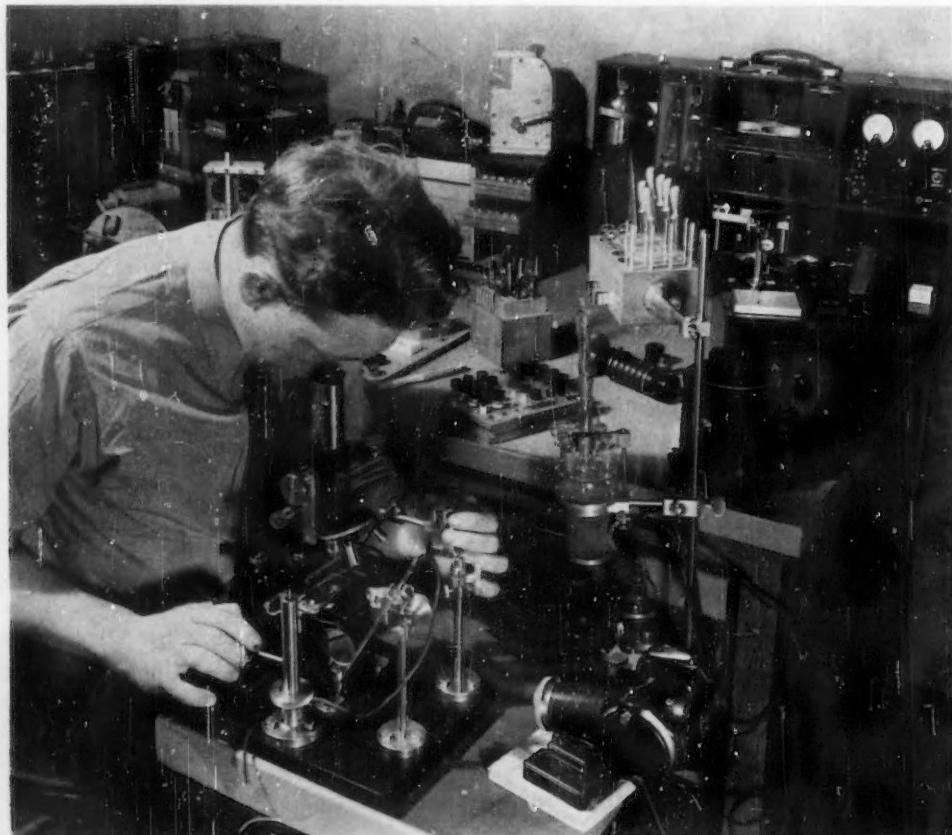


Fig. 1.—Portable Microchemical Laboratory Setup in a Telephone Central Office.

paratus, and they instigated the building of the Kuhlmann microbalance which would weigh with sufficient accuracy samples in the microgram region.

But these pioneers, and those who have followed them in the ensuing thirty years, found that the matter was not so simple as that. Two difficulties have continually arisen when the scale of analytical operations was reduced: the inadequacy of some of the classical methods of laboratory manipulation, and the necessity for new instruments to aid sensory perception. It is the success that has attended efforts to surmount these difficulties that justifies the assignment of a special and important place to microanalysis in modern analytical chemistry. It is much more than merely the carrying out of standard analytical procedures on small samples through the employment of miniature, doll-house apparatus; it embodies principles, points of view and objectives, as well as apparatus and techniques, that make it, rather, an altogether new kind of analysis.

Filtration is a good example of a manipulation that cannot be successfully carried out on a microscale by the classical method. The macroanalyst with 50 or 100 ml. of a suspension that he wishes to filter, pours it through the familiar cone-shaped folded filter held in a funnel. The microanalyst with, say, 0.5 ml. of suspension finds that he cannot successfully effect filtration by using a funnel and filter proportionately reduced in size. The suspension crawls over the edge of the funnel, for example, to such an extent that a prohibitive amount of the precipitate is lost; and he is not able to control the operation on this scale so that this and other objectionable things do not happen. So he has devised entirely new techniques. In one of these a microbeaker, having a weight not incomensurate with that of the precipitate eventually to be weighed, is used as the reaction vessel. This is weighed on the microbalance before the analysis, together with a device called a filter stick. The latter is essentially an inverted micro-Büchner funnel made of glass or porcelain, about as long as the microbeaker is high, so that it fits inside and reaches to the bottom; the filtering agent may be any of the usual ones—paper pulp, asbestos, sintered glass, etc. The great advantage of this method of filtration is that all of the steps in the analysis are carried out in the single vessel. After the precipitation is made, the filter stick is inserted and the filtrate then drawn off by suction; the precipitate may be washed in the same manner. Finally the whole system, beaker plus filter stick plus precipitate, is dried and weighed and the weight of the precipitate obtained of course by difference.

It was stated that analysts formerly suffered from the lack of suitable chemical reactions. In choosing the compound in which he is to weigh the element to be determined, the gravimetric analyst always has preferred, other things being equal, that compound in which the element sought contributes the smallest fraction to the total molecular weight; or, to put it another way, that which gives the highest degree of "chemical amplification." The reason for this is of course that the higher the amplification the smaller is the effect of errors in weighing on the final result. In macroanalysis this was of relatively small importance, because the amount of the end product to be weighed could be made large enough to compensate for an unfavorable amplification factor. But micro-



Fig. 2.—Portable Electrographic Equipment for Studying Contamination of Dial Apparatus Contacts *in situ*.

analysts with their limited samples could not do this. Therefore they have made intensive search for reactions which resulted in products having high amplification factors for the elements to be determined. A good example of such a product is sodium zinc uranyl acetate by the formation of which sodium may be determined and which contains only about 1.5 per cent of that element, thus giving a seventy-fold amplification.

The need for aids to sensory perception, or, one might say, for making the senses more acute, has been felt very strongly in microanalysis. And workers in this field have not hesitated to appropriate to their needs instruments developed for this purpose by scientists in other branches. The most obvious and important means for extending one of the senses is the microscope, and Chamot and Mason at Cornell University, by their work in chemical microscopy, have made contributions to microtechnique second in importance only to those of Pregl and Emich. But besides microscopes of various kinds, the modern microchemical laboratory contains such nonchemical equipment as dental drills, medical school dissecting instruments, and micro-manipulators. We have even devised a "sniffer" for assisting the nose to smell. In fact, instrumental aids are lacking only for the sense of taste.

In 1925 Dr. J. B. Niederl and Dr. A. A. Benedetti-Pichler, who had been students of Emich and Pregl, organized the first courses in microchemistry in America at New York University. Twelve years later, in 1937, reports Frank Schneider,<sup>3</sup> there were at least forty educational institutions in this country offering such courses, and the figure is doubtless substantially larger by now. Schneider also

<sup>3</sup> *Mikrochemie*, Vol. 22, p. 265 (1937).

reported that there were twenty-one seats of microchemical instruction in Europe, a figure that has probably dipped close to zero by this time.

About ten years ago the Bell Telephone Laboratories organized what was probably the first extensive microchemical laboratory in American industry. At that time the dial system of telephone switching was coming into wide use. This system is characterized by a large number of small parts, rather delicately articulated both mechanically and electrically, and comprising a considerable number of chemically different materials. As was inevitable, trouble arose from time to time with the apparatus in the dial central offices, and the trouble frequently was of a chemical nature. It thus became necessary to provide facilities and techniques for making what might be called microchemical diagnoses in such cases, and microanalysis, concentrating as it does not only on small samples but on carrying out operations on small areas and on a reduced manipulative scale, offered a promising approach.

The work of the Bell Laboratories microchemists is by no means limited to making analyses by the classical Pregl and Emich techniques; that is merely the nucleus, around which have grown a host of other techniques drawn or adapted from other fields or devised by us. "Samples" submitted to these specialists lack the simplicity and homogeneity of samples typically sent to an analytical laboratory; and the questions asked them go far beyond those ordinarily asked an analyst. For example, this "microchemical diagnostician" may be handed a telephone relay—a rather complex piece of apparatus—with some such request as this: "This relay has failed in service. We have examined it electrically and mechanically and cannot find the cause of failure; we believe the cause is chemical. Please find out what caused this relay to fail; tell us, if possible, how it can be repaired; and advise what changes we should make in design or manufacturing practice to avoid such failures in the future product." Very obviously, the wisdom, skill, and knowledge necessary to answer such questions are of an altogether different brand from those required to analyze a steel sample for carbon.

This kind of chemical work may also be compared to that of the scientific criminologist. Like him, our microchemists see no reason to limit themselves to any particular group of techniques or instruments; the objective is to find the answer in the most efficient manner, and what methods are used is immaterial. It has worked out, however, that the principles of microchemistry have, as a body, proved more useful in this chemical detective work than have those of any other branch of chemistry. Carrying the analogy further, our microchemists, like the criminal investigator, have concluded that, when possible, the best place to work is at the scene of the crime. If a piece of dial



Fig. 3.—Portable Microchemical Laboratory Packed in Cases for Transportation.

apparatus that has got into trouble in a certain central office is the object of attention, rather than have the apparatus removed and sent in to the laboratory, it is better to take the laboratory to the central office and there examine the "sample" in its natural environment. To this end, we have designed and built a portable field microchemical laboratory which can be set up in a central office and with which we can perform most of the operations that we can in our permanent laboratory as effectively if not always as conveniently.

In the past ten years, scores of industrial laboratories have equipped themselves for microchemical work, and many have provided elaborate facilities. The general recognition of the importance of microchemistry is attested by the formation, several years ago, by the American Chemical Society of a Microchemical Division (now the Division of Analytical and Microchemistry), coordinate with such venerable divisions as that of organic chemistry. At a recent general meeting of that society more than 250 persons attended the 18 sessions of the Microchemical Division. On the reasonable assumption that about 25 per cent of the membership of the American Chemical Society attends its semiannual meetings, that indicates that there are in the United States at least one thousand people who are actively interested in microchemistry, and the number is growing rapidly.

## Electronic Instruments in Analysis, Testing, and Control

By Ralph H. Müller<sup>1</sup>

THE CLASSICAL methods of physical chemistry have been employed in analytical chemistry for many years. Some of these methods were so convenient and reliable that they were adopted by industry for the con-

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tinuous recording and control of the particular variable. This was true of thermal conductance of gases, the pH of solutions, and the thermoelectric measurement of temperature. Many other methods have remained comparatively unused and still retain a certain "research aspect,"

either on account of the elaborate apparatus which is necessary or because they require elaborate control of auxiliary factors such as temperature. The use of the glass electrode is a good example of this situation. Until recently, the use of the glass electrode required a delicate quadrant electrometer, elaborate electrical shielding, and the general precautions which were reminiscent of a research problem in atomic structure.

The increasing use of electron tubes is rapidly changing the entire picture. The early applications represented a direct substitution of an electron tube for one of the components of the standard apparatus with some increase in sensitivity and convenience. The present trends are in the direction of "all electronic" components, and in many cases entirely new methods have been evolved.

The first electron tubes were far from uniform; they were erratic and short lived. Even for the less exacting demands of radio communication, they were far from satisfactory. The enormous magnitude of the modern radio industry has accounted for such fundamental and technical advances in tube manufacture that it may be said with certainty that the average electron tube possesses characteristics which are as reproducible and reliable as many of the ordinary pieces of equipment which one finds in the laboratory, such as thermometers and volumetric glassware. Just as these common commodities are subject to careful calibration if precise or referee values are required, so the electron tube may be incorporated in a circuit where its performance may be checked or monitored.

A cardinal virtue of any well-designed instrument is its ability to supply the desired information with little or no computation. In pure research, a morning may be devoted to gathering data and the afternoon and half the night to calculations, but in general this cannot be tolerated in practical or control work. The instrument should be direct reading. No small amount of ingenuity has been exercised, in the past, in incorporating calculating mechanisms in instruments, especially in industrial recorders. The solutions have usually been mechanical, that is, with the use of appropriately cut cams and levers. Electron tubes and their associated circuits provide unlimited possibilities. Simple examples are functional relationships involving the logarithmic, reciprocal, polynomial, and functions related to the conic sections. Many specific applications may be mentioned: the square-law detector, the logarithmic vacuum tube voltmeter, vacuum tube watt meter, and direct reading conductance meter. While it might be inferred that no great reliance could be placed on a tube for performing these mathematical functions, it is always possible to include self-checking means within the circuit.

As specific examples of the application of electronic methods, we might discuss electrometric titrations. Practically all vacuum tube voltmeters that are used for this purpose are of the slide-back variety, that is, the emf. of the electrode system is applied to the input terminals of the electronic tube in series with a potentiometer. The potential which is set on the latter is adjusted in magnitude until it is equal and opposite to the unknown potential. The vacuum tube is therefore used solely as a criterion of the equality of the two potentials. A characteristic limitation of such equipment has been the need

for plotting the entire titration curve. This handicap to routine application has been eliminated in two general ways. The circuit of Garman and Droz provides such high sensitivity, without danger of overloading the instrument, that the instrumental indication can be made equal to the full scale value for the addition of one drop of reagent at the end point. An electronic approach is available in the circuit of Baker and Müller which is the electrical equivalent of the well-known method of differential titrations. In this case no signal is obtained except in the immediate vicinity of the end point.

Corresponding simplifications in the field of conductance measurements have not been forthcoming, but from the present state of the electronic art it may be expected that equally simple means will soon be devised. Notable improvements in Wheatstone bridge circuits have already enriched the general technique, and electronic circuits furnishing reciprocal resistance readings have been devised. For the present, it is still necessary to plot the results in order to locate the end point in a titration.

The use of dielectric constant measurements is not so widespread as their precision and simplicity would seem to warrant. This is probably due to the fact that most measurements have been made by the heterodyne beat method, for which the measuring equipment is very complex. New developments with high-Q resonant circuits have provided a very simple means for very accurate measurement of dielectric constants. Due to the very high dielectric constant of water it would seem that this technique would be entirely suited for the measurement of purity of organic liquids. It has already been used extensively in routine or control methods for the inspection of such materials as lumber, cereals, and tobacco.

Photometric methods of analysis and control are based almost entirely in modern technique on the use of some variety of photoelectric cell. The apparent simplicity of the barrier-layer type has accounted for the predominance of this type in photometric work. The unwarranted suspicion attached to the more complicated combination of vacuum cell and amplifier is rapidly disappearing. Primarily with the aid of this combination we are witnessing the appearance of high precision photometers and spectrophotometers. The most recent of these includes a photoelectric photometer reading directly in extinction values, and therefore directly proportional to the concentration of the colored solution, with complete interlock of all optical and electrical adjustments. The direct reading feature is accomplished by means of slide-back vacuum tube voltmeter with logarithmic input compensation. Complete stability is available, even under line operation, by electrical compensation methods, whereby the small increase in luminosity of the light source is compensated by an equal decrease in the high voltage supply to the amplifier.

The cathode ray oscilloscope finds many applications in analysis and control. Its general ability to measure phenomena of extremely short duration may be utilized in a number of ways. With appropriate resonant networks, it may be used to detect small differences in the magnetic properties of ferrous alloys, and wherever such differences can be unmistakably correlated with differences in composition, such measurements may be used analytically.

# Theory and Practice of pH Determination and Control Using the Glass Electrode<sup>1</sup>

By Malcolm Dole<sup>2</sup>

THE FIRST SIGNIFICANT work on the glass electrode was done by Haber of synthetic ammonia fame and his student Klemensiewicz in the year 1909; but, probably because of the Great World War, no subsequent studies of the glass electrode worth mentioning were made until the period beginning in 1924 when Brown and Kerridge, working in A. V. Hill's laboratory of physiology at the University of London, developed a practical glass electrode cell for the purpose of measuring the pH of biological fluids. In 1929 and to the present time, the most important glass electrode researches have been carried on in America, beginning with the development at the Rockefeller Institute for Medical Research of the proper type of glass to use and at Northwestern University of an adequate theory of the electrode in the light of its limitations. Goodhue, working at Iowa State College at Ames, demonstrated that a small, compact, and portable glass electrode pH outfit could be constructed using low cost thermionic vacuum tubes and a condenser in the amplifying part of the circuit. The development of similar reliable, convenient, and relatively inexpensive pH meters on a commercial basis has made possible the rapid growth in the use of the glass electrode which we see today.

The chief advantage of the glass electrode as a pH indicating device rests in the fact that the electron does not take part in the electrochemical reaction occurring at the surface of the sensitive glass when the minute current flows on making the emf. or pH measurement. For this reason, other possible electrode reactions involving electrons, such as oxidation-reduction reactions, discharge of oxygen, reduction of unsaturated hydrocarbons, etc., which so disturb pH measurements with the hydrogen or quinhydrone electrodes, do not interfere with glass electrode pH measurements, allowing the glass electrode to be applied to all kinds of aqueous systems, heterogeneous as well as homogeneous. There are, however, certain limitations to the glass electrode which will be described below.

Glass electrodes are always made of Corning 015 glass which has the composition 72 per cent SiO<sub>2</sub>, 6 per cent CaO, and 22 per cent Na<sub>2</sub>O—the glass MacInnes and Dole found to be best for pH measurements.<sup>3</sup>

Recently Beckman and his coworkers at the National Technical Laboratories in Pasadena have discovered a glass,

their number 4990E, which is considerably superior to the Corning 015 glass for pH measurements in the high pH range, up to pH 13 or 14. The greater electrical resistance of this glass, however, discourages its use for general pH measurements.

Although glass electrodes can be made in a variety of shapes and sizes, the most common form is the simple bulb type originally studied by Haber and Klemensiewicz<sup>4</sup> which is illustrated complete with inner reference solution and electrode in Fig. 1 (a). Figure 1 (b) is a similar type as used in some commercial pH electrometers with the Corning 015 glass on the bottom part of the bulb only as indicated by the dotted line. Figures 1 (c) and (d) are two types of the MacInnes and Dole thin membrane electrode.<sup>5</sup> Electrodes (c), (d), (g), (e), (h), and (k) are particularly suitable for the measurement of the pH of small quantities of fluids; electrodes (i), (j), and (l) are rugged electrodes with the Corning 015 glass held in a protected position and are, therefore, not easily broken. Electrode (l) is a spear type electrode for the measurement of the pH of butter, meats, and muscle tissue, substances into which the electrode must be pushed (in the case of meat or muscle an incision is made with a knife before trying to insert the electrode).<sup>6</sup>

Cells to hold the glass electrode and the reference electrode, which is usually a saturated calomel reference electrode, are similar to cells employing the hydrogen or quinhydrone electrode; however, the design of microcells is simpler in the case of the glass electrode, as the rigorous exclusion of air is usually not necessary. The importance of methods of forming the liquid junction and the magnitude of its potential are frequently overlooked, yet for

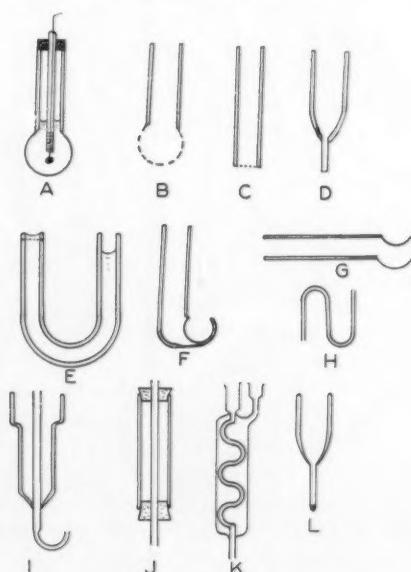


Fig. 1.—Various Types of Glass Electrodes.

<sup>1</sup> For a complete discussion of the glass electrode including methods, applications, and theory see the forthcoming monograph by the author, "The Glass Electrode," to be published by John Wiley and Sons, Inc., New York, N. Y.

<sup>2</sup> Associate Professor, Research Laboratory of Physical Chemistry, Northwestern University, Evanston, Ill.

<sup>3</sup> D. A. MacInnes and M. Dole, *Journal, Am. Chemical Soc.*, Vol. 52, p. 29 (1930).

<sup>4</sup> F. Haber and Z. Klemensiewicz, *Zeitschrift für physikalische Chemie*, Vol. 67, p. 385 (1909).

<sup>5</sup> D. A. MacInnes and M. Dole, *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 1, p. 57 (1929).

<sup>6</sup> References and a more detailed discussion of electrodes and complete cells are given in the author's forthcoming monograph.

accurate measurements the uncertainty in the liquid junction potential may be the limiting factor. As pointed out by a number of people, the liquid junction should not be formed within the pores of a ground glass stopper, nor should the saturated potassium chloride salt bridge solution meet the test sample at the tip of a capillary tube. For reproducibility it is essential that the junction have "cylindrical symmetry"; that is, the junction should be formed within a tube so that diffusion will take place linearly.

It is a great temptation to go only as far as to read the pH off the dial of commercial instruments without questioning the accuracy and reproducibility of the liquid junction potential; merely estimating the pH on the dial to 0.01 pH gives us, unfortunately, no surety that we have really measured the pH that accurately.

The older emf. measuring circuits which made use of quadrant or Lindemann electrometers have been displaced at the present time by the more accurate, cheaper, and more convenient thermionic amplifying circuits. The technique of constructing satisfactory amplifiers such as the DuBridge and Brown circuit employing the General Electric FP-54 tube has become so standardized that a capable first year graduate student can now build such an instrument in two or three months and have it work correctly the first time tried. The new synthetic plastics such as Lucite, Amphenol, and Bakelite, to mention a few trade names, serve as excellent materials out of which switches, insulators, coaxial shielded and insulated cables, and vacuum tube sockets can be fabricated. Figure 2 illustrates probably the most satisfactory wiring diagram for an amplifying circuit, that of DuBridge and Brown<sup>7</sup> with a few slight modifications. For accuracy to  $\pm 0.1$  mv., the galvanometer should have a sensitivity of  $5 \times 10^{-10}$  amp. per mm. scale deflection at 1 meter. Particular attention should be given to the insulation and shielding of the input circuit and switch. In case money is available for the purchase of one of the many excellent commercial pH meters now on the market, it would be unnecessary to construct such an outfit, unless the highest accuracy and stability are desired. It should also be mentioned that pH meters for the automatic recording or control of pH are now manufactured by several different industrial concerns.

Among the many types of industrial applications of the glass electrode we can point to its application in the food

industry and the leather and rubber industries as being of first importance. In the determination of the pH of canned fruit juices, the glass electrode is not subject to the poisoning effect of ascorbic acid as is the quinhydrone electrode, nor do the potentials of the glass electrode drift with time as is the case with the quinhydrone electrode in canned chocolate syrup or in canned grapefruit, orange juice, lemon juice, prunes, etc. The convenience and speed of pH measurement with the glass electrode in one instance enabled the pH of over 400 different samples of root beer to be measured in a week with one machine; a single measurement can be made—not too accurately, to be sure—within two minutes. By slicing open a steak or a cheese the pH of these semisolid substances can be determined, usually with a spear-type electrode.

Rubber and leather are two substances whose preparation and properties depend markedly on the hydrogen ion concentration of the medium from which they are precipitated; for this reason we have found the chemists in the leather industry to be among the first in leading the industrial development of the glass electrode. Probably the glass electrode is the only instrument by which the pH of tanning liquor extracts or of rubber latex can be accurately measured. Other important uses of the glass electrode are to be seen in pH measurements of soils, silicate solutions, sulfite liquors, hypochlorite bleaching liquors, dyeing baths, soap solutions, plating baths, gels, colloidal suspensions, emulsions, beer, whiskey, and ore flotation agents. It should be pointed out that for many of these substances, indeed for most of them, the glass electrode method is the only one by which the pH may be measured, or reliably measured. Now that Beckman and his coworkers have discovered a new type of glass which is much less affected by sodium ions in solutions of high pH than is Corning 015 glass, the useful pH range of the glass electrode has been materially extended. We also wish to emphasize the fact that the glass electrode has found extensive application in the biological sciences, with such diverse systems as the brain, the skin, muscle tissue, the saliva, the stomach, and the blood coming into the realm of pH investigation.

Despite the extensive application of the glass electrode, there are difficulties in its operation, some easily overcome but others inherent in the instrument itself. Because of the high electrical resistance of the thin glass membrane, the special thermionic amplifying circuits mentioned above must be used to measure the emf.; because of the fragility of the thin glass wall, reasonable care must be exercised in using the glass electrode. In potentiometric titrations in which the glass electrode is placed directly in the liquid to be analyzed, a guard ring, now commercially available, should be placed about the electrode to prevent it from being accidentally hit by the stirring rod. Because of the high soda content of the glass, the membrane slowly gives off alkali, requiring pH measurements of pure water, of unbuffered salt solutions, or of small amounts of liquid to be carried out rapidly or on flowing solutions. If the pH of the system is not more alkaline than 7, the Corning 015 glass can be replaced by a chemically more resistant glass, such as ordinary soft glass which would not as rapidly contaminate the solution with alkali. At ele-

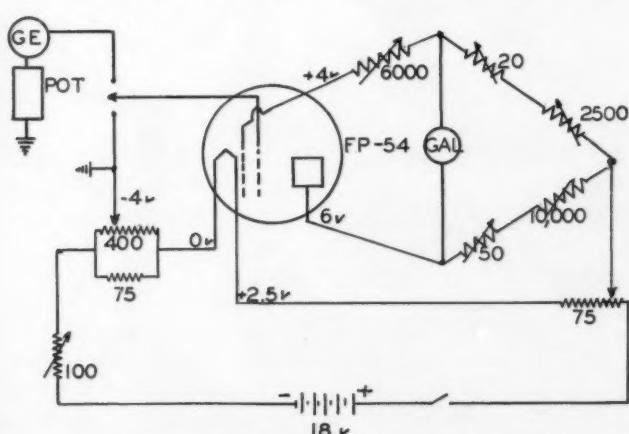


Fig. 2.—Internally Compensated Circuit of DuBridge and Brown.

<sup>7</sup> L. A. DuBridge and H. Brown, *Review of Scientific Instruments*, Vol. 4, p. 532 (1933).

vated temperatures, from 80 to 100 C., the Corning 015 glass gives trouble because of the attack of the glass by the solution and should be replaced by a more resistant glass. Dr. Beckman and his coworkers at the National Technical Laboratories, Pasadena, have developed special glass electrodes for high-temperature pH measurements.

Because of the low concentration of hydrogen ions in basic solutions, sodium ions or other cations take part in the electrochemical reaction at the glass surface, thus producing a change in free energy different from that of a true hydrogen electrode and giving rise to an error of pH measurement. The sodium error, so-called, which may be as large as one whole pH unit or larger, can be considerably reduced by using the special glass developed by Dr. Beckman and his associates. This sodium error is greater, the greater the pH, the larger the sodium ion concentration, and at any given pH it increases rapidly with increase of temperature. However, the pH of basic solutions falls with rising temperature so that the sodium error for any given solution does not rise as rapidly with rise of temperature as might be expected.

If the vapor pressure of the water in contact with the glass membrane is lower than that of pure water, as it is in strongly acid, concentrated salt, or nonaqueous solutions, the pH given by Corning 015 glass electrodes is higher than it should be. Thus the glass electrode is limited in its applicability to aqueous solutions having pH values greater than zero. Both the sodium errors and the vapor pressure lowering errors may be calculated if the composition of the solution is known and a correction applied to the observed pH, the uncertainty concerning the correction factor being greater the greater the deviation of the glass electrode from its true hydrogen electrode function.

Hydrogen fluoride or fluoride salt solutions below a pH of 6 or 7, depending on the fluoride concentration, attack the glass causing perceptible errors.

We come finally to the theory of the glass electrode. In the limited space at our disposal we are unable to elaborate the mathematical details of the present accepted theory; nevertheless we shall attempt a brief discussion of the fundamental ideas involved. Thermodynamics teaches us that the free energy decrease of a spontaneous chemical or electrochemical process depends only on the initial and final state of the system and is independent of the path by which the system passes between these two states. Consequently for the emf. (apart from the asymmetry potential) across the glass membrane to be equal to that given by two hydrogen electrodes placed in solutions of

the same pH, it is necessary that as the current flows through the two types of cell the same net electrochemical reaction take place in each case. Since we know that hydrogen electrodes transfer hydrogen ions, in the form of hydrogen gas, from the more concentrated to the more dilute solution, one equivalent per faraday, it follows that the glass membrane must also transfer one equivalent of hydrogen ions per faraday of electricity passed through the cell. But we know further that electrical conduction through glass is not electronic, but electrolytic; hence we believe that hydrogen ions are transferred across the glass membrane as such without ever becoming molecular hydrogen gas. This important difference in the mechanism of the hydrogen ion transfer, which can be described essentially as the nonparticipation of electrons in the glass electrode reaction and which is of great practical importance, explains the complete indifference of the glass electrode to oxidation-reduction potentials existing in the solution and to all possible electrochemical reactions involving electrons.

In basic solutions, hydrogen ions existing in the surface structure of the glass probably are replaced by sodium ions of the aqueous solution as the concentration of the sodium ions of the solution may be  $10^9$  to  $10^{14}$  times greater than the concentration of the hydrogen ions. The glass electrode emf. then becomes a function of the sodium ion concentration of the solution; the free energy decrease of the electrochemical reaction across the glass membrane no longer equals that of a pair of hydrogen electrodes; and the glass electrode fails to give the correct hydrogen electrode emf. The pH reading is too low. This metallic ion error depends on the type of ion present as well as upon its concentration and pH, sodium and lithium ions being the worse offenders; divalent ions or large univalent ions like the tetraalkyl ammonium ions produce little error. As stated above, the sodium error can be nearly eliminated by the use of the new Beckman glass.

The hydrogen ion probably does not take part in the electrochemical reaction as an unhydrated proton or hydrogen atom as it must in the ordinary platinum electrode reaction, but as a proton hydrated with one molecule of water,  $H_3O^+$ . If this is the case, water as well as hydrogen would be transferred by the electrode reaction giving rise to an extraneous free energy contribution if the activity of the water, or its vapor pressure, is lowered in the solution on one side of the glass membrane. The behavior of the glass electrode in highly acid solutions appears to agree with the quantitative expectations of this theory.

## Dimethylglyoxime and the General Use of Organic Precipitants in Inorganic Analysis

By Harvey Diehl<sup>1</sup>

WITH RESPECT to the techniques employed or the problems to which they are applied, there are no essential differences in the use of inorganic and organic compounds as precipitating agents in analysis. With both types of reagents there arise the same problems of

proper sampling, the dissolution of the sample, the adjustment of the various conditions of valence state, acidity, and temperature prior to the precipitation, and the same final operations of filtering, igniting, and weighing. Thus, any arbitrary division of the field of inorganic analysis into organic reagents and inorganic reagents is

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meaningless, except possibly as a convenience for those pursuing investigational work in the field. There has been a tendency toward the creation of such a division in recent years because of the signal success of certain organic precipitants, but a little reflection will show that many inorganic reagents are just as effective and specific, the chloride ion, for example, which under the correct conditions precipitates only silver. But the vast realm of organic compounds has been but little explored for precipitating agents, and for those who would extend the boundaries of inorganic analytical chemistry, it is an intriguing and fruitful region for research.

Of the organic compounds which have so far been examined for their behavior toward the metals, dimethylglyoxime has been the most spectacular in action and of the greatest utility in practice. This reagent is so selective in action and so unique in character that it serves as a guiding light to other similar reagents and furnishes a beautiful example both of what such reagents may accomplish and the limitations to which they are subject. For this reason the major part of this paper will be devoted to dimethylglyoxime and its uses, particularly as they illustrate the general field, and the latter part will deal with a few other reagents and the sources of information regarding them.

#### DIMETHYLGlyOXIME

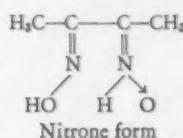
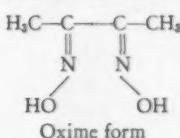
It is now about thirty-five years since the reaction of dimethylglyoxime with nickel salts was first observed by the Russian chemist, Tschugaeff, and utilized in the analysis of nickel by the German, Brunck. The unique nature of the dimethylglyoxime-nickel reaction made its use quickly universal, and it is interesting to note that when the European supply was cut off by the World War, dimethylglyoxime was among the first of the compounds whose synthesis on a larger scale was undertaken in the laboratories of the University of Illinois. The synthesis used was published in a form which was shortly afterward adopted by *Organic Syntheses*, and the manufacture was quickly taken over by the chemical sales division of the Eastman Kodak Co. and others.

During the period of 1905 to 1925 a number of investigations were made on the applications of dimethylglyoxime, and the use of this reagent has now become so common that many things are taken for granted that are not actually justified.

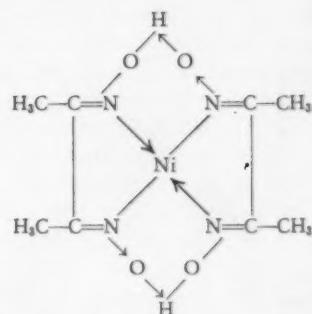
First, however, consider the structure of nickel dimethylglyoxime. This is no ordinary salt but what is termed an *inner complex* compound, a metallic derivative of an organic molecule in which the metal is a member of a ring structure and the compound as a whole is a non-electrolyte. The metal atom in such a compound is completely surrounded by the organic molecule and since the new molecule carries a zero charge, it is essentially non-polar in nature and the properties normally characteristic of the salts of the metal disappear. Such compounds are insoluble in aqueous solutions; on the other hand they are soluble in organic liquids. They exhibit remarkable stability and they possess striking colors which depart widely from the colors of the normal salts of the metal. These properties make them ideally suited to the purposes of analytical chemistry.

Older ideas pictured nickel dimethylglyoxime as a six-

membered ring, but as a result of a number of lines of reasoning, the structure of this compound is now thought to be a five-membered ring. One of the oxime groups of the dimethylglyoxime molecule undergoes a shift to the tautomeric nitrone form:

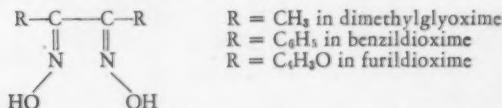


in which form it functions as an acid, the hydrogen atom being replaced by the nickel atom. The nickel atom also becomes attached to the second oxime group giving the structure

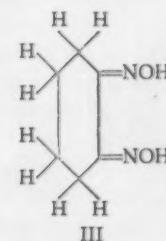
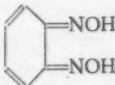


The four bonds attaching the nickel atom are covalent or nonionic, and identical except that two have been formed with the replacement of a hydrogen atom. The arrow represents a so-called *semipolar* double bond and also a *coordinate* bond, such as exist in the salt hydrates and the ammoniates. The hydrogen atoms of the two oxime groups are further bound to oxygen atoms and made nonreactive.

The methyl groups of the dimethylglyoxime molecule may be replaced by other radicals



without disrupting the ability to form red insoluble nickel derivatives. The aromatic compounds orthobenzoquinonedioxime (I) and naphthaquinonedioxime (II)



are strong dibasic acids but are not specific in action, forming precipitates with many metals. Cyclohexanedionedioxime (III) is apparently aliphatic in nature and functions like dimethylglyoxime. It has certain advantages, having a high molecular weight and being water-soluble. When made available, this reagent should replace dimethylglyoxime.

The precipitation of nickel with dimethylglyoxime occurs in a neutral, ammoniacal, or very weakly acidic solution. The precipitate is flocculent in nature but filters

without much difficulty. The compound is definite in composition and stable toward heat so that it may be dried at 120°C. and weighed. None of the common metals yields precipitates with dimethylglyoxime, and the method serves to separate nickel from practically everything. In the presence of iron it is necessary to add some reagent which will prevent the precipitation of ferric hydroxide or basic acetate. Tartaric acid is most commonly added for this purpose, and it similarly prevents the precipitation of aluminum and chromium. This makes possible the direct determination of nickel in steel, and the advent of dimethylglyoxime greatly simplified and improved this important determination.

Among the points which have been commonly overlooked in connection with the determination of nickel in this manner is the solubility of nickel dimethylglyoxime. Brunck very early emphasized that the solution must be cooled before filtering. However, a number of modern texts prescribe that the solution be filtered hot and washed with hot water. Recent data covering this point show that this error may amount to several milligrams and that it is definitely necessary to cool the solution at least 1 hr. and to use cold water for transferring the precipitate (7).<sup>2</sup> The precipitate, in common with other inner complex compounds, has an appreciable solubility in organic solvents, in alcohol, and also in ether, so that these solvents must not be used for washing the precipitate as is frequently recommended.

The solubility of the precipitate in chloroform is so great that small amounts of nickel may be extracted from aqueous solutions by chloroform. This has recently been used by Sandell for the recovery of the small amounts of nickel in silicate rock (2). The chloroform extract was subsequently treated with hydrochloric acid, which returns the nickel to the aqueous phase where it can be determined colorimetrically.

Dimethylglyoxime is only slightly soluble in water, so that the reagent must be made up in alcohol or acetone, and there is the danger that the reagent itself will be precipitated when added to the aqueous solution, thus contaminating the nickel precipitate. This is a serious defect but not a fatal one since the solubility of dimethylglyoxime is about 40 mg. per 100 ml. of water and in the presence of alcohol is still greater, so that a small excess of the reagent may be added safely. The permissible excess varies with the acidity and temperature of the solution and with the amount of reagent used, that is, the amount of alcohol or acetone added, so that no rule may be stated; in general, a 5- to 10-ml. excess of a 1 per cent solution is safe.

Oxidizing agents in ammoniacal solution produce with nickel and dimethylglyoxime a quadrivalent nickel compound having the composition  $\text{NiD}_2\text{O}$ , where D indicates a molecule of dimethylglyoxime minus one hydrogen atom. The material is orange to brown in color and is soluble. There are two phases of the reaction of importance to the analyst. The first of these is the loss of nickel when precipitated in the presence of oxidizing agents. Low results are obtained in the presence of ferricyanide, manganic compounds, permanganate, and similar oxidizing agents. The effect of nitrate upon the determination has been in some doubt. Feigl, discussing the effect of oxidizing

agents, about 1924 (3), states that Brunck, who did much of the early work on the determination of nickel, found that the presence of nitrate prevented the complete deposition of nickel. A search of Brunck's papers reveals no such statement, although it is found that Brunck did confine his work entirely to chloride and sulfate solutions. After running a series of nickel determinations under various conditions with and without nitrate we have concluded that it has no effect, at least when the amount of nickel is above a few milligrams. Nor were we able to find nickel in the filtrate using the more sensitive colorimetric method (4). On the other hand, small amounts of nickel are definitely not precipitated by dimethylglyoxime. This was reported several years ago by Harwood and Theobald (5) who were unable to detect nickel known to be present in silicate rock. Again, Jones (6) found that amounts of nickel less than 0.06 per cent in steel are not precipitated by dimethylglyoxime and may be found in the filtrate. Jones went into this matter in great detail and found that quite frequently appreciable amounts of nickel have been reported as only traces.

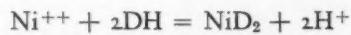
Fortunately the colorimetric method, just referred to, works nicely over this lower range of concentration of nickel. This is based on the soluble, orange-brown, quadrivalent nickel compound of dimethylglyoxime just mentioned. The determination is easily carried out. The solution is simply treated with bromine water and dimethylglyoxime, made ammoniacal, and then compared with standards. Jones applied this method to the determination of small amounts of nickel in iron and steel. For the separation of nickel from iron, Jones used a modified hydroxide precipitation which is very good. It is well known, of course, that iron cannot be separated from nickel, cobalt, and zinc by precipitation with ammonia; even several reprecipitations do not free the iron from all of the other metals. Jones neutralized the solution to the point where the iron was just about to precipitate, then added cyanide. The cyanide ties the bivalent metals up in very stable complex ions from which they are not precipitated on the addition of ammonia. At no time, then, during the subsequent precipitation of iron with ammonia are the bivalent metals precipitated as hydroxides and the question of their being leached from the ferric hydroxide precipitate by the excess of ammonia never enters. Copper, cobalt, and nickel are then found in the filtrate and the colorimetric method can be applied directly. Small amounts of copper do not interfere and larger amounts can be removed by a sulfide precipitation. Amounts of nickel in the range of 0.005 to 0.1 mg. may be determined by this method. A large sample, say 4 g., may be taken and the method speeded up by diluting the solution containing the ferric hydroxide precipitate to a definite volume. The volume of the precipitate is neglected, the solution filtered through a fluted filter, and an aliquot of the filtrate taken for the colorimetric determination. Jones used hypochlorite for the oxidizing agent but hypobromite is equally satisfactory. The color is fairly stable and easily matched. We have found the method very satisfactory and have been able to determine nickel in about 45 min. The colorimetric method was also used by Sandell to determine the nickel in silicate rock following its isolation by the chloroform extraction method mentioned earlier.

<sup>2</sup> The italic numbers in parentheses refer to the reports and papers appearing in the list of references appended to this paper.

Another interesting note in this connection is the determination of biacetyl, the flavoring matter of butter and of coffee. Biacetyl can be isolated by steam distillation, and treatment with hydroxylamine converts it to dimethylglyoxime. This is then determined by adding a nickel salt and hypobromite which produces the orange-brown quadrivalent nickel compound which is then compared with standards. It is necessary first to remove the excess hydroxylamine; this is easily done by the addition of a nitrite, the excess of which is then removed by urea. The results have been excellent (7).

Another curious phase of the determination of nickel using dimethylglyoxime is the separation of cobalt and iron. Cobalt and dimethylglyoxime form soluble compounds, brown or green in color, and if sufficient dimethylglyoxime is added to combine with both the nickel and cobalt the separation of nickel from cobalt works nicely. And as mentioned, if tartrate is present, nickel can be separated from iron. If both iron and cobalt are present, however, there is produced a slimy brown precipitate which contaminates the nickel deposit and renders filtration practically impossible. This precipitate has been shown to be a compound containing one atom of iron, one atom of cobalt, and three molecules of dimethylglyoxime (8). The determination of nickel in cobalt steels thus becomes something of a problem; and the importance of cobalt steels and the newer magnetic alloys of cobalt, nickel, iron, and aluminum make its solution increasingly desirable. Brunck, himself, first suggested the way to handle this situation (9), and the facts just mentioned and the Brunck method were rediscovered by Balz (10) some 20 years later. By reducing the iron to the ferrous state, conveniently with sulfite, and maintaining a reducing solution throughout the determination, the trouble is completely eliminated. Ferrous iron is not precipitated from an ammoniacal tartrate solution by dimethylglyoxime, cobalt forms amino compounds, and the nickel dimethylglyoxime precipitates completely in pure form. There is another possible method of doing this, but the reduction process just described is the most convenient.

An interesting volumetric method for nickel is possible using dimethylglyoxime. The precipitation of the nickel derivative is accompanied by the liberation of two hydrogen atoms



Holluta (11) some 20 years ago titrated these hydrogens with a standard base, using methyl orange as indicator. The procedure was limited to a very few milligrams of nickel because the bulk and color of the precipitate obscured the end point. If this could be done potentiometrically, the method might be suitable for the determination of fairly large amounts of nickel. This is actually the case (4). It is possible to determine even 250 mg. of nickel using either the antimony or quinhydrone electrode. The original solution is titrated with sodium hydroxide, giving a sharp break, at which point a turbidity of nickel hydroxide just appears. A measured small amount of standard acid is then added to dissolve the precipitate of hydroxide, the dimethylglyoxime is added, and the acid liberated is titrated with a base. Equilibrium is established quite rapidly and the second break is quite sharp. By this scheme we were able to obtain acceptable

results on pure nickel solutions. Unfortunately, when tartaric acid is present a buffering action sets in and the break is flattened out so that the titration is of no value; there is undoubtedly a complex of some sort produced between the nickel and the tartaric acid, which behaves as a very weak acid. The addition of glycerol to a pure nickel solution does not affect the titration. If iron is present, however, the buffering action again occurs and no end point can be found. This method is therefore of no value for the determination of nickel in steel.

Another volumetric method, based on the determination of the hydroxylamine liberated when the nickel dimethylglyoxime precipitate is dissolved in acid and the dioxime decomposed, has been proposed (12) but has not been much used. It appears to offer distinct possibilities however.

Dimethylglyoxime also precipitates palladium, forming a yellow compound which is insoluble even in dilute mineral acid solutions. The nature of the compound is strictly analogous to that formed with nickel. This furnishes an excellent method for the separation and determination of palladium (13).

Platinum is partially precipitated by the reagent on boiling, either as the metal or as a greenish complex compound. Gold is reduced to the metal but this reaction is not much used for other reducing agents are available which give a better precipitate and a cleaner separation.

Ferrous iron reacts with dimethylglyoxime in the presence of ammonia to give a rose-red coloration. This has frequently been mistaken for nickel. Nickel always appears as a precipitate, however, while the ferrous compound is soluble and fades on contact with air. This test is an extremely sensitive one for ferrous iron, being capable of detecting 1 part of iron in 20,000,000. This would probably be a satisfactory method for the colorimetric determination of iron. Tschugaeff (14) has already supplied some of the details for this, but another investigation in light of the modern knowledge of colorimetry would be desirable.

Copper, dimethylglyoxime, and certain oxidizing agents, such as persulfate and silver or periodate, in alkaline solution produce a purple coloration, resembling permanganate. This is an extremely sensitive test for copper and is suitable for its colorimetric determination, the details having been worked out by Hurd and Chambers (15) and by Kolthoff (16).

Hot solutions of bismuth salts when treated with dimethylglyoxime and made strongly alkaline yield a yellow precipitate. This is a sensitive test for bismuth. The presence of tartrate inhibits the reaction so that bismuth does not interfere in the analysis of nickel.

Still another reaction which should receive some attention is that of cobalt salts with dimethylglyoxime when an aromatic amine, such as benzidine, is present. A deep brown color is formed, by which as little as 0.5 microgram of cobalt may be detected. This reaction would probably be an excellent colorimetric method for cobalt.

Besides the determination of nickel, then, dimethylglyoxime has a number of uses: in the determination of palladium, the colorimetric determination of iron and copper, and in the detection of bismuth and cobalt. Its prime use is, of course, still in the determination of nickel. Here, however, a few points should be kept in

mind: the solubility of the precipitate in hot water and in organic solvents, the failure of small amounts of nickel to precipitate, the effect of oxidizing agents, the valuable colorimetric method for small amounts of nickel, and the coprecipitation of iron and cobalt when present together.

#### CUPFERRON, 8-HYDROXYQUINOLINE, AND OTHER REAGENTS

It will not be possible in this paper to go into detail about other reagents as we have with dimethylglyoxime. The number of satisfactory organic precipitants known is not large. A few of the reagents have been known for some time and are in common use—cupferron, 8-hydroxyquinoline, and alpha-nitroso-beta-naphthol being among these. Several other reagents have certain merits which indicate that they will receive increasing attention, among them alpha-benzoinoxime and para-hydroxyphenylarsonic acid. A variety of others have been insufficiently studied or publicized or have some fatal defect which limits their use. Each of these reagents could bear extensive further study and important uses may be found for them.

Known almost as long as dimethylglyoxime is the reagent ammonium para-nitrosophenylhydroxylamine, discovered by Baudisch, and given the name cupferron. Not as specific in action as dimethylglyoxime, cupferron precipitates copper, iron, titanium, zirconium, vanadium, thorium, tin, bismuth, mercury, and gallium, which effects important separations of these metals from aluminum, chromium, manganese, nickel, and the like. The reagent is not stable in hot solutions, and unfortunately the precipitates are of indefinite composition and must be ignited to the oxides for weighing. The newer reagent, neo-cupferron, the naphthyl homologue of cupferron, forms less soluble precipitates and makes possible the direct separation of iron and copper from mineral waters. A complete treatment of the preparation and storage of the reagent, the solubilities of cupferron metal compounds, the analytical application of the reagent, and a comprehensive bibliography may be found in the monograph, "Cupferron and Neo-Cupferron" by Smith (17).

The reagent 8-hydroxyquinoline, like dimethylglyoxime yields inner complex compounds with a number of metals. Control of the pH of the solution is essential for the separation of the bivalent metals by this reagent. The important uses of 8-hydroxyquinoline to date have been in the separation of iron and aluminum from phosphate and beryllium, and in the determination of magnesium. 8-hydroxyquinoline may be determined by a bromine titration and, since its precipitates with the metals are soluble in mineral acids, this affords a good indirect volumetric method for such metals as magnesium and aluminum for which volumetric methods are lacking. The work on 8-hydroxyquinoline is summarized in the book by Berg, "Das O-Oxychinolin" (18).

Alpha-benzoinoxime is more or less specific for copper in ammoniacal solutions containing tartrate, yielding a green, slightly soluble copper salt which separates copper from many of the common metals. The separation from iron is not entirely satisfactory, the precipitate being difficult to filter and badly contaminated. From mineral acid solutions benzoinoxime precipitates molybdate, tungstate, and a few other anions, and the reagent has been applied successfully to the determination of molybdenum in steel (19).

The arsonic acid grouping,  $\text{AsO}_3\text{H}_2^-$ , is specific for metals of the fourth group of the periodic table, particularly for the A subgroup and tin. Investigations by Chandlee and his coworkers (20) have shown how the behavior varies in an interesting manner with the nature of the radical attached to the arsonic acid group. Para-hydroxyphenylarsonic acid,  $\text{HOCH}_2\text{C}_6\text{H}_4\text{AsO}_3\text{H}_2$ , is a particularly good reagent, giving a separation of titanium and zirconium from all of the common metals but tin. The precipitates are ignited to the oxides for weighing.

#### GENERAL BIBLIOGRAPHY AND CONCLUSION

The theoretical aspects of the subject of organic analytical reagents have been dealt with in a number of places. The introductory chapters of Feigl's now classical "Tüpfelanalyse" (21) constitute probably the most extensive reference.

Among the pioneering works of Feigl should be noted particularly his researches dealing with the specific reactivity of certain atomic groupings, and his work dealing with the increase in sensitivity with increasing weight and by the introduction of color into the organic compound. A guide to the original literature on these subjects will be found in the chapters mentioned.

The staff of the British firm of Hopkin and Williams, Ltd. has pursued researches on organic reagents for metals and has published its findings in book form, now in its fourth edition (22). The work of these chemists has been devoted largely to testing the various reagents and checking their usefulness both from qualitative and quantitative viewpoints. The results of these investigations together with a critical review of the literature are given in the brochure.

The German monograph series, "Die Chemische Analyse," carries two volumes of interest in this field, "Das O-Oxychinolin" by Berg, already mentioned, and "Organische Fällungsmittel in der Quantitativen Analyse" by Prodinger. The latter has recently been translated into English (23), and besides sections devoted to such better known reagents as 8-hydroxyquinoline, cupferron, and dithizone, it deals with a number of reagents which have received less attention, such as anthranilic and quinaldic acids and benzmercaptothiazole, which appear to have certain uses.

The last five years have seen two group efforts toward the systematic investigation of organic compounds for their utility in analytical chemistry. The first of these was international in scope, being composed of Feigl of Vienna, Nieuwenburg of Delft, Böttger of Leipzig, Komarovsky of Odessa, and Stafford of Manchester. The effort was devoted entirely to testing the reagents for their qualitative uses, but the entire field of known reagents was covered and excellent data were obtained on the sensitivity of the reagents, the type, color, and other characteristics of the reactions and the interfering ions. The work has been summarized in the "Tables of Reagents" (24), a curious volume which has parallel passages in three languages but which is written in a highly condensed and tabular form employing a symbolism which is a happy blend of French, German, and English, making a sort of international scientific jargon which is perhaps the first of its kind.

A more recent group effort has been led by Yoe of the

University of Virginia and the first results of this work have been presented in a recent symposium (25). This work has consisted in testing a great number and variety of organic compounds for color and precipitation reactions with the metals.

It will be gathered from the foregoing review that the general field of applying the numerous organic compounds to inorganic analysis is attracting more and more attention, and that a great body of work is accumulating dealing with the various phases of the problem. Concerning any one reagent there is a great deal to learn, particularly of its behavior on the complex mixtures encountered more commonly than not in practice. The nature of the atomic groupings that have specific affinities for this or that metal, which is the primary problem, is gradually being elucidated. The equally important related problems, the possibility of alternative volumetric methods, the adequate study of the materials which interfere, the conditions of pH and temperature at which precipitation is made, and similar factors, are more carefully being taken into account; and the various limitations as to size of sample, solubility of the reagent itself, solubility of the precipitate in organic solvents, and the possibility of using this solubility as an extraction method for effecting separation are now more fully appreciated. Progress is perhaps slower and less spectacular than the optimist might expect or the practicing analyst desire, but is steady and of great promise.

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## Tetravalent Cerium and Its Use in Volumetric Analysis

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**T**HE USE OF TETRAVALENT cerium in volumetric analysis constitutes one of the outstanding recent advances in analytical chemistry. Summaries of developments in this field, including extensive bibliographies, have been made at frequent intervals (1-4).<sup>3</sup> Newer developments have resulted in improved methods of preparation of the reagents employed. The theoretical background has been materially altered, clarified, and rationalized. The field of application has been extended, and the older methods simplified and improved. It is the purpose of the present paper to again summarize the field in the light of these newer studies.

*Advantages in the Use of Cerium in Volumetric Analysis.*—A list of advantages in the use of tetravalent cerium in volumetric analysis includes:

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<sup>3</sup> The italic numbers in parentheses refer to the reports and papers appearing in the list of references appended to this paper.

1. A wide range of oxidation potentials is available, depending upon conditions selected. The normal oxidation potentials cover the entire range from 1.28 v. in 1 M hydrochloric acid solution to 1.86 v. in 8 M perchloric acid solution (5).

2. Solutions of tetravalent cerium are satisfactorily stable over the entire range of available oxidation potentials (6, 7). Solutions in sulfuric acid are completely stable for indefinite periods of time under ordinary conditions, and at the boiling point for short periods of time. Solutions in hydrochloric acid of moderate concentration are probably equally stable at ordinary temperatures. Solutions in nitric acid and perchloric acid compare favorably with those of permanganate in neutral solution (of which the oxidation potential is lower).

3. But a single electron exchange is possible, namely, tetravalent to trivalent cerium. This fact liberalizes the conditions of applicability without encountering disturbing side reactions.

4. A wide variety of reactions has been described, and newer methods are constantly being devised.

5. The best standards of reference, such as sodium oxalate and arsenious oxide, may be employed in the evaluation of tetravalent cerium solutions.

6. Hydrochloric, sulfuric, nitric, or perchloric acid solutions of tetravalent cerium can be used in oxidations and in the preparation of solutions for analysis.

7. Titrations of excess tetravalent cerium, in procedures involving excess of oxidant and back-titration, give a definite color change which serves as a warning of the approach to the equivalence point.

8. Ferroin, nitro-farroin, and other high potential internal indicators which are reversible and of a vivid color change are available for practically all reactions.

9. A tetravalent cerium salt has been prepared which is suitable for use as a standard of reference (8), ammonium hexanitrate-cerate ( $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ ). A new standard of reference, potassium sulfato-cerate ( $\text{K}_2\text{Ce}(\text{SO}_4)_3$ ), is about to be described also.

10. The standard solutions required are easily prepared from a variety of starting materials.

11. Tetravalent cerium solutions are not highly colored, which facilitates the reading of calibration on standard volumetric apparatus, and solutions of cerous salts are colorless, which is advantageous in the use of internal indicators.

12. Convenient methods of electrolytic oxidation of trivalent to tetravalent cerium under a wide variety of conditions and by the use of a wide variety of electrode materials at high current efficiencies have been developed (9).

*Disadvantages in the Use of Cerium in Volumetric Analysis.*—A list of disadvantages in the use of tetravalent cerium in volumetric analysis includes:

1. The high equivalent weight of the reagents employed is coupled with a comparatively high cost.

2. Reactions in slightly acid, neutral, or alkaline solution are not available.

3. The use of a catalyst is frequently required.

4. Reactions of tetravalent cerium in hydrochloric acid solution are of low potential as compared to permanganate. Reactions in the presence of sulfuric acid do not equal corresponding permanganate reactions in potential.

5. Reverse titrations following the use of excess tetravalent cerium are not permissible in the presence of phosphates.

6. A more extensive selection of applicable internal indicators is desirable.

*Ceric Oxide Recovery from Cerium Ores.*—Ceric oxide is the most convenient source of raw material for use in the manufacture of salts for application to analysis. The simplest procedure for the preparation of the thorium-free cerium group oxides (10) involves the formation of a double sulfate with sodium sulfate, starting with monazite sand. The ceric oxide thus prepared contains lanthanum, praseodymium, neodymium, samarium, and possibly europium, gadolinium, and terbium. A further purification results in the elimination of the associated elements as hereinafter referred to (8).

Ceric oxide in various degrees of purity, essentially free from thorium oxide, but containing 5 to 60 per cent of the

other cerium group metal oxides, is marketed at present. The chief uses for these products are in ceramics for the manufacture of colored glazes, in the manufacture of electric arc carbons to provide more brilliant flaming arcs, and in the manufacture of pyrophoric alloys for use in military pyrotechnics and kindred applications. The uses in analytical chemistry are rapidly assuming considerable proportions, as are industrial applications such as in the development of color in dyes fixed to textiles in the reduced form. The cost of ceric oxide, depending upon the cerium content, varies from 60 to 80 cents per pound for a 40 per cent oxide to \$2.50 per pound for a 90 to 95 per cent content.

*Preparations of Tetravalent Cerium Salts from Ceric Oxide.*—The most important preparations of tetravalent cerium salts are listed in Table I.

TABLE I.—COMMERCIALLY AVAILABLE TETRAVALENT AND TRIVALENT CERIUM SALTS.

Purity 90 to 100 per cent; contaminants, cerium group metals.

Chemical Name	Formula	Molecular Weight
Ceric oxide	$\text{CeO}_2$	172.13
Tetraammonium sulfato-cerate dihydrate	$(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$	632.57
Ammonium nitro-cerate	$(\text{NH}_4)\text{Ce}(\text{NO}_3)_6$	548.27
Potassium nitro-cerate	$\text{K}_2\text{Ce}(\text{NO}_3)_6$	590.39
Ceric sulfate (anhydrous)	$\text{Ce}(\text{SO}_4)_2$	332.25
Cerous sulfate (hydrated)	$\text{Ce}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	730.58
Cerous nitrate (hydrated)	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	434.25
Cerous perchlorate (hydrated)	$\text{Ce}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$	338.51
0.5 M Perchlorato-ceric acid in 6 M perchloric acid	$\text{H}_2\text{Ce}(\text{ClO}_4)_2$	738.91

Solutions of tetravalent cerium for use in volumetric analysis may be prepared from the materials listed in Table I by solution in acids of chosen strength, or they may be prepared by electrolytic oxidation (9).

*The Electrolytic Oxidation of Cerous Salts to the Corresponding Ceric Acids.*—The electrolytic oxidation of cerium has been described by Hengstenberger (11). Following his procedure, a diaphragm cell using a platinum anode and cathode was employed. Based upon the knowledge that tetravalent cerium exists as an anion rather than a cation, the use of a diaphragm might logically be considered unnecessary. Such was found to be the case (9).

As electrode materials, platinum anodes and cathodes are to be preferred. Lead dioxide anodes deposited on platinum are suitable for use in the oxidation of cerous sulfate in sulfuric acid solution in the preparation of sulfato-ceric acid but are too greatly attacked in the preparation of nitro- or perchlorato-ceric acids. Cathodes may be either of lead or of platinum. In all cases the ratio of the area of anode to cathode should be at least 100 to 1. The voltage across the cell terminals should be maintained at 3.2 to 3.5 v., and current densities of from 0.7 to 7 amp. per sq. in. may be employed without need for cooling the cell. Oxidations may be 98 to 100 per cent complete, and the current efficiency is almost 100 per cent up to 80 per cent oxidation. Cerous sulfate can be completely oxidized at approximately 75 per cent current efficiency.

The oxidation of cerous perchlorate in perchloric acid solution to perchlorato-ceric acid constitutes the only known satisfactory method for the preparation of this product. The electrolytic oxidation of cerous chloride to chloro-ceric acid ( $\text{H}_2\text{CeCl}_6$ ) must be accomplished by using a diaphragm cell. The most practical procedure for the preparation of pure ceric sulfate or ammonium sulfato-cerate is based on the preparation of pure ammonium

nitrato-cerate from low grade ceric oxides (8), followed by reduction to cerous nitrate and ammonium nitrate with hydrogen peroxide, and precipitation as cerous sulfate. The reoxidation of the cerium is carried out electrolytically as just described. Details of a few electrolytic oxidations are given in Table II.

TABLE II.—THE ELECTROLYTIC OXIDATION OF CEROUS SULFATE, NITRATE, AND PERCHLORATE IN SULFURIC, NITRIC, AND PERCHLORIC ACID SOLUTIONS WITHOUT THE USE OF A DIAPHRAGM CELL.

Current density 0.069 amp. per sq. in. at the anode and 6.67 amp. per sq. in. at the cathode. Voltage, anode to cathode, 3.5 v.

Electrolyte	Percentage Oxidized	Final Normality	Current Efficiency for 80 per cent Oxidation
0.2526 M $\text{Ce}_2(\text{SO}_4)_3$ in 1.5 M $\text{H}_2\text{SO}_4$	100	0.5051	89.36
0.510 M $\text{Ce}(\text{NO}_3)_3$ in 2.0 M $\text{HNO}_3$	99.7	0.5087	84.44
0.522 M $\text{Ce}(\text{ClO}_4)_3$ in 6.0 M $\text{HClO}_4$	98.9	0.5087	96.91

*Determination of Molal Electrode Potentials of the System Tetravalent-Trivalent Cerium in Hydrochloric, Sulfuric, Nitric, and Perchloric Acid Solutions.*—Cerous chloride, sulfate, nitrate, and perchlorate were prepared from pure  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ , and the corresponding acids of tetravalent cerium ( $\text{H}_2\text{CeCl}_6$ ,  $\text{H}_2\text{Ce}(\text{SO}_4)_3$ ,  $\text{H}_2\text{Ce}(\text{NO}_3)_6$ , and  $\text{H}_2\text{Ce}(\text{ClO}_4)_3$ ) were prepared by electrolytic oxidation as previously described. In the electrolytic oxidation of cerous chloride a diaphragm cell was employed. The solutions of tetravalent cerium were analyzed to find the extent of oxidation and, in case one or two per cent of trivalent cerium remained, appropriate correction was made.

Solutions of the above formulated cerium acids were then prepared in the corresponding acids in 1, 2, 4, 6, and 8 molal strength (1 M only in case of  $\text{H}_2\text{CeCl}_6$ , since stronger hydrochloric acid causes precipitation). The single-electrode potential in each case was determined as follows: A known volume of solution was reduced by adding hydrogen peroxide, determining the exact point of complete reduction potentiometrically. The proper quantity of the same ceric solution was then added to produce a ratio of 1 to 1 of reduced and of oxidized cerium in the solutions of known free acid content. In the hydrochloric and sulfuric acid solutions, the saturated calomel electrode was used as reference with platinum as the other electrode. In the nitric and perchloric acid solutions, a saturated sodium nitrate or sodium perchlorate salt bridge was interposed between the saturated calomel electrode and the cell liquid to establish the 1 to 1 ratio of oxidized and reduced cerium, and the salt bridge was removed for reading the adjusted solution potential. This was done to prevent error from diffusion of chloride into the cell, which is easily oxidized in the case of a nitric or perchloric acid solution of tetravalent cerium. The final reading in direct contact with the saturated calomel cell was taken because of the unknown liquid junction potential from the salt bridge. Details of the potentiometer circuit are omitted, since an accuracy of greater than 0.01 v. is not

claimed for these measurements. The results are shown in Table III.

The results of Table III for molal  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  are in agreement with published results (12, 13).

#### POTENTIOMETRIC TITRATIONS

*Ferrous Iron by Ceric Cerium.*—The ferrous solutions were adjusted to approximately 0.05 N in concentration of the corresponding acids. The ceric solutions in 1 N sulfuric and hydrochloric acids were prepared as previously described. The nitric and perchloric acid solutions, 1 N in acid and approximately 0.05 N in ferrous nitrate and perchlorate, were similarly titrated using ceric solutions which were approximately 0.05 N in oxidizing value and 1 N in the corresponding acids. In the latter cases, the potentiometric titration was carried out using a platinum electrode and the saturated calomel electrode, but with a saturated sodium nitrate or sodium perchlorate salt bridge. The potentials were corrected for the salt bridge contact potential by eliminating the salt bridge at the completion of the titration and determining the change in potential.

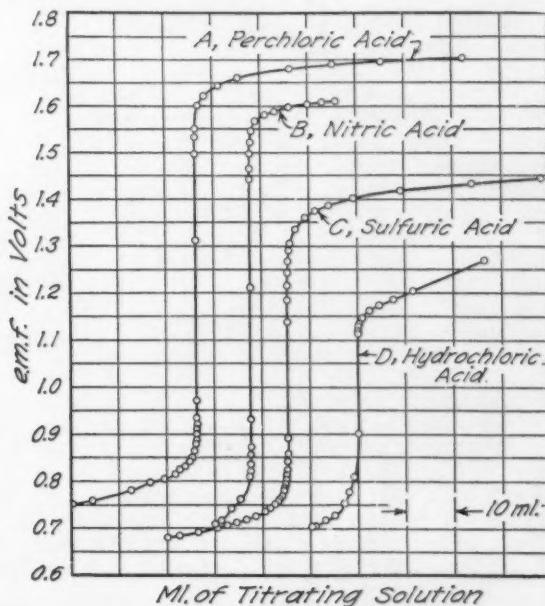


Fig. 1.—Potentiometric Titration of Ferrous Iron in Normal Perchloric, Sulfuric, Nitric, and Hydrochloric Acids.

The results are shown graphically in Fig. 1. The potentials are given as the ordinates calculated to the basis of the normal hydrogen electrode. Curves A, B, C, and D are, respectively, those for the perchloric, nitric, sulfuric, and hydrochloric acid solutions. In each curve the value for the single-electrode potential of the normal ferrous-ferric system is the first point plotted at the left end of the curve and corresponds to a ferric-ferrous ratio of 1 to 1. The last point on each curve to the right corresponds to the single-electrode potential for the various systems at which the ratio of tetravalent to trivalent cerium is 1 to 1.

*The Titration of Ferrous Perchlorate at Increasing Concentrations of Perchloric Acid.*—These potentiometric titrations will show the advantage resulting from the increase in oxidation potential as influenced by increase in the acid strength employed.

TABLE III.—SINGLE-ELECTRODE POTENTIAL VALUES OF  $\text{Ce}^{++++}/\text{Ce}^{+++}$  SYSTEM.

Acid Concentration	Electrode Potentials in Volts with Reference to Normal Hydrogen Electrode			
	$\text{HClO}_4$ Solution	$\text{HNO}_3$ Solution	$\text{H}_2\text{SO}_4$ Solution	HCl Solution
1 M	1.70	1.61	1.44	1.28
2 M	1.71	1.62	1.44	...
4 M	1.75	1.61	1.43	...
6 M	1.82	1.56	1.42	...
8 M	1.87	1.56	1.42	...

Ferrous perchlorate solutions in 1, 2, 4, 6, and 8 N perchloric acid were titrated using solutions of approximately 0.05 N tetravalent cerium in the corresponding concentrations of perchloric acid. The solutions were prepared and the titration performed under the same conditions as previously described. The data are shown graphically in Fig. 2. The values for the single-electrode potential of the ferric-ferrous system increase with increase in normality of perchloric acid from the normal value of approximately 0.75 v. to approximately 0.88 v. at 8 N perchloric acid strength. The values at the points corresponding to equal concentrations of tetravalent and trivalent cerium agree well with those given in Table III, which were determined in the absence of iron as previously described. At the end of each titration the addition of 5 to 10 ml. of concentrated sulfuric acid instantly lowered the potential nearly to the much lower values obtained for the sulfuric acid titrations described below.

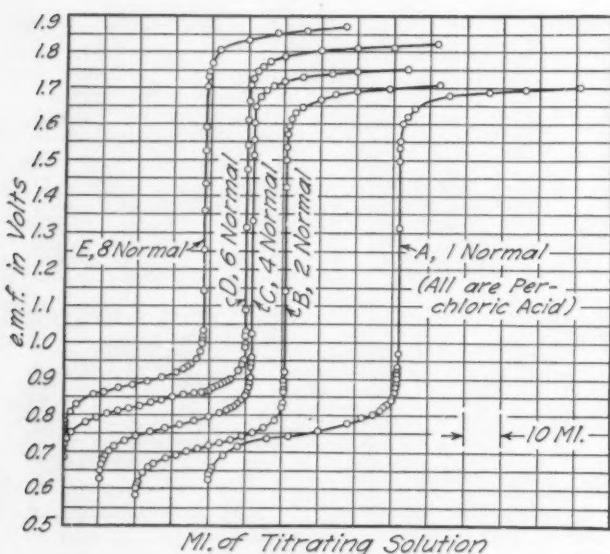


Fig. 2.—Titration of Ferrous Perchlorate at 1 to 8 N Perchloric Acid Strength.

*The Simultaneous Oxidation of Ferrous and Vanadyl Perchlorates in Strong Perchloric Acid Solution.*—A practical application of cerate oxidation in strong solutions of perchloric acid is the determination of mixtures of ferrous and vanadyl ions. Using 8 molal perchloric acid solutions, the ferric-ferrous potential was found to be 0.825 v. and the vanadic-vanadyl system was found to be 1.23 v. The  $[Ce(ClO_4)_6^{4-}]/[Ce^{4+}]$  potential was found to be approximately 1.8 v. The "break" in potential for both the iron and vanadium determination was found to be approximately 300 mv. The reaction is fast in attaining equilibrium. Such titrations show the possibility of extending the practical working range into the materially higher potential field through use of the cerate ion in strong perchloric acid solution. A series of oxidations of organic compounds under somewhat the same conditions will illustrate the advantages as hereinafter described.

*The Early Theoretical Interpretation of Ceric Oxidimetry.*—The early studies of the procedures of ceric oxidimetry

lead to the assumption of a simple  $Ce^{4+}/Ce^{3+}$  ratio of oxidant to reductant. The following are some of the major objections to this concept:

1. The wide variation in the normal single-electrode potentials shown in the data of Table III cannot be satisfactorily explained on the basis of hydrolysis to form complex cations such as  $(CeOH^{3+})$  as postulated by Noyes and Garner (13).

2. These oxidation potentials should not be materially altered by change in the acid concentration or changes in the concentration of the acid anions concerned. The electrode potentials are observed to decrease (Table III) with increase in concentration of nitric and sulfuric acids, but increase markedly with increase in perchloric acid concentration. The same effect in the latter case can be brought about by addition of  $NaClO_4$  in equal strength.

3. The high single-electrode potentials attained in perchloric or nitric acid solutions can be immediately lowered to potentials approaching those characteristic of sulfuric acid solution by the addition of sulfuric acid in amounts equivalent to the perchloric or nitric acid present.

4. The electrode potentials in sulfuric acid solution can be materially increased, although to a lesser degree than the effect noted under 3 above, by the addition of nitric or perchloric acid.

5. Cerous sulfate, nitrate, and perchlorate can be quantitatively oxidized to the corresponding acids ( $H_2Ce(SO_4)_3$ ,  $H_2Ce(NO_3)_3$ , and  $H_2Ce(ClO_4)_6$ ) using an electrolytic oxidation cell without diaphragm. This fact eliminates from consideration any appreciable concentration of  $Ce^{4+}$  ions and shows that the  $Ce(SO_4)_3^{4-}$ ,  $Ce(NO_3)_3^{4-}$ , and  $Ce(ClO_4)_6^{4-}$  anions are not appreciably dissociated in solutions containing molal concentrations or more of the corresponding acids.

*The Newer Interpretation of Ceric Oxidimetry Called Cerate Oxidimetry.*—The experimental work of Meyer and Jacoby (14) on the preparation and properties of ammonium hexanitratocerate indicates that this product is a complex salt dissociating in solution to give ammonium ions and nitratocerate ions.

Since the single-electrode potential of this salt at standard state in nitric acid solution is the same as that of cerous nitrate after electrolytic oxidation in 1 M nitric acid, both solutions can be said to owe their oxidizing value to the same ion species. Ceric nitrate in nitric acid solution is then in reality hexanitratoceric acid,  $H_2Ce(NO_3)_6$ . This product, like its ammonium salt, dissociates in solution to give mainly the nitratocerate ion,  $Ce(NO_3)_6^{4-}$ , and hydrogen ions. The ceric-cerous electrode potential relationship instead of a simple  $Ce^{4+}/Ce^{3+}$  ratio should be formulated as follows:

$$\frac{[Ce(NO_3)_6^{4-}]}{[Ce^{4+}][NO_3]_6^4} \dots \dots \dots \quad (1)$$

The extent to which tetravalent cerium enters the complex nitratocerate ion is a function of the nitrate ion concentration. The potential of this system at 2 M nitric acid concentration is 1.62 v., which corresponds to the presence of all or most of the tetravalent cerium in the complex nitratocerate ion. With further increase in nitrate ion concentration the potential decreases, as would be

predicted from an increase in the nitrate ion concentration in the denominator of the above ratio, until at 8 M nitrate ion concentration the potential has decreased to 1.56 v.

Similar reasoning can be applied to electrolytically oxidized cerous perchlorate in perchloric acid solution. The ceric-cerous electrode potential follows the concept of the perchlorato-cerate ion ratio to the product of the cerous and perchlorate ions:

$$\frac{[\text{Ce}(\text{ClO}_4)_6^{--}]}{[\text{Ce}^{+++}] [\text{ClO}_4^-]^6} \dots \dots \dots \quad (2)$$

The degree to which the tetravalent cerium is found as the complex perchlorato-cerate ion is again a function of the perchlorate ion concentration. The highest degree of complex ion formation as shown in Table III has not been attained at 6 or even 8 M perchloric acid strength. At 8 M perchloric acid strength the potential of this system is still increasing, as shown in Fig. 1. Increasing the perchlorate ion concentration continues to increase the oxidation potential, as the denominator effect is less than that caused by the continued increase in the complexing of the tetravalent cerium.

The ionic relationship expressed in Ratio 2 can be converted in large part to that of Ratio 1 by the addition of the nitrate ion. In this case the potential of the system decreases.

By analogous reasoning the conditions involving ceric ion in sulfuric and hydrochloric acid solutions are expressed by the following electrode potential ratios:

$$\frac{[\text{Ce}(\text{SO}_4)_3^{--}]}{[\text{Ce}^{+++}] [\text{SO}_4^{--}]^3} \dots \dots \dots \quad (3)$$

$$\frac{[\text{CeCl}_6^{--}]}{[\text{Ce}^{+++}] [\text{Cl}^-]^6} \dots \dots \dots \quad (4)$$

In ceric solutions at 1 M sulfuric acid concentration the degree of formation of cerate ions is at its maximum, since further addition of sulfuric acid only lowers the potentials of the system. The existence of the complex sulfato-cerate ion was postulated by Jones and Soper (15).

*The Preparation, Standardization, and Stability of Perchlorato- and Nitrato-Cerate Solution.*—Solutions of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  in perchloric acid of from 1 to 8 molar strength are the equivalent of perchlorato-ceric acid ( $\text{H}_2\text{Ce}(\text{ClO}_4)_6$ ) prepared by electrolytic oxidation of cerous perchlorate. The procedure for the preparation of such solutions is to add the required amount of ammonium nitrato-cerate to the calculated amount of 72 per cent perchloric acid and dilute to volume with vigorous agitation and slow increase in volume.

The equivalent of a solution of sulfato-ceric acid ( $\text{H}_4\text{Ce}(\text{SO}_4)_4$ ) is made by the addition of ammonium nitrato-cerate to concentrated sulfuric acid, followed by slow dilution and vigorous agitation. The potentials of the solution thus prepared are the same as would result from the solution of  $\text{Ce}(\text{SO}_4)_2$  or of  $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$  in the corresponding strength of sulfuric acid. They are as stable upon boiling for short periods of time as those described by Willard and Young (16).

The potentials attained by the perchlorato- and nitrato-cerate ions in nitric and perchloric acid solutions are so high (1.6 to 1.87 v.) that some instability upon storage would be expected. Carbon or platinum black and to a

lesser extent bright platinum catalyze this decomposition. The reaction is comparatively rapid in the former two cases. It is also well to store the solutions in the dark, although the solutions are not appreciably sensitive to light. Under proper conditions, standard solutions of the cerate ion in nitric or perchloric acid need not be restandardized more frequently than every 10 to 15 days, as shown by Smith and Getz (17).

The usual standards of reference— $\text{Na}_2\text{C}_2\text{O}_4$ ,  $\text{As}_2\text{O}_3$ ,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , or pure iron—may be used. Smith and Getz found all of these to be applicable (18). The use of sodium oxalate in titration in either direction is particularly recommended, using nitro-ferroin as indicator. This is the only standard volumetric oxidation of sodium oxalate that can be carried out at ordinary temperatures. The potential change at the equivalence point is over 600 mv. The reaction is advantageous in the indirect determination of calcium following precipitation as oxalate, as has been demonstrated in a series of unpublished results.

*The Oxidation of Organic Compounds Using Tetravalent Cerium.*—The most generally applicable procedure for the oxidation of organic compounds is by the use of permanganate in strongly alkaline solution. This procedure was developed by H. Stamm and the best outline of the procedure is to be found in Bottger's text as translated by Oesper (19). The method is of wide application and has the advantage that the results are stoichiometric and not empirical. Organic compounds containing aliphatic double bonds, or alcoholic or phenol ( $\text{OH}^-$ ) groups, or amines, or carboxyl groups are oxidized to  $\text{CO}_2$  and water. A list of materials quantitatively oxidized by alkaline permanganate includes, among others, methanol, formic acid, and phenol.

It is beyond the scope of this particular subject matter to discuss the Stamm procedure in detail, but it may be said to have several serious objections. The permanganate is reduced to manganate, and conditions have to be somewhat rigidly controlled to avoid oxidation as a side reaction by the latter. The determination of the excess permanganate involves some considerable difficulties since barium salts must be added to prevent reactions of the manganate formed through the formation of alkali-insoluble barium manganate. The determination of permanganate in alkaline solution involves titration with sodium formate, and it is necessary to run blank determinations to evaluate correction factors. A catalyst has to be employed. Other objections could be mentioned, but the procedure has at least the distinction that it is not empirical and high equivalent weights are the usual rule. In general, the limit of accuracy is approximately 0.5 per cent.

Ceric sulfate has been proposed by Willard and Young (20) for use in the determination of a limited group of organic compounds. An excess of standard ceric sulfate is added to a sulfuric acid solution of the organic material to be oxidized (15 to 75 ml. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.5) in 100 to 300 ml. of solution). The solution mixture thus prepared is held at 90 to 95 C. for periods of time varying between 10 and 120 min., depending upon the material being oxidized. The resulting solutions are then cooled to room temperature and the excess ceric sulfate back-titrated, using standard ferrous sulfate with ferroin as indicator.

The reaction mechanism resulting from this procedure

TABLE IV.—THE DETERMINATION OF ORGANIC ACIDS USING EXCESS STANDARD CERIC SULFATE AND BACK-TITRATION (THE WILLARD AND YOUNG PROCEDURE).

Organic Acid	Sample Range, g.	H <sub>2</sub> SO <sub>4</sub> (sp. gr. 1.5), ml.	Time, min. at 90 to 95 C.	Volume of Solution, ml.	0.1 N Ce <sup>++++</sup> , ml.	Weight of Acid, g. per ml. of 0.1 N Ce <sup>++</sup>	Equivalents of Ce <sup>++++</sup> per Mole of Acid
Tartaric	0.0213-0.1598	15 to 45	10 to 60	100 to 300	30 to 100	0.002084	7.2
Malonic	0.0173-0.0867	20 to 80	15 to 60	80 to 400	35 to 100	0.001563	6.66
Malic	0.0338-0.0593	20 to 60	15 to 120	200	50 to 75	0.001449	9.25
Glycollic	0.1026-0.2005	20 to 60	30 to 120	100 to 300	50 to 75	0.001923	3.95
Citric	0.0500-0.0700	20 to 75	30 to 60	100 to 300	60 to 100	0.001211	15.85

is unknown. The reaction products, unlike those in Stamm's alkaline permanganate method (19), are not almost exclusively  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , but, instead, formic acid is in general the end product. The results obtained are in all cases empirical in nature, but with careful control of the reaction conditions, the results attained can be precisely reproduced. For those compounds to which the method applies, the procedure is to be preferred to Stamm's alkaline permanganate method, but the number of tested applications are not so numerous.

A tabular summary of the conditions for the application of the Willard and Young procedure is given in Table IV.

The action of sulfuric acid solutions of ceric sulfate is negligible, under the conditions of the Willard and Young procedure, on formic, acetic, and succinic acids, and but slight on fumaric and maleic acids. Benzoic, phthalic, and salicylic acids are partially and variably oxidized. The list of determinations outlined in Table IV does not include polyhydric alcohols, pentoses and hexoses, or disaccharides, which can be determined by the alkaline permanganate method. A procedure for the determination of glucose, fructose, and invert sugars is that of Whitmeyer (21). In this case the reducing sugar is oxidized in the presence of sodium carbonate by use of an excess of potassium ferricyanide. The solution is then acidified, and the ferrocyanide formed in the reaction is titrated with ceric sulfate. Alphazurine G is used as indicator, the color change being from yellow-brown to green. The alkaline copper sulfate procedure for the oxidation of reducing sugars, in which the cuprous oxide precipitate is dissolved in a measured excess of standard ceric sulfate and the excess back-titrated with ferrous sulfate using ferroin as indicator, has been developed by Stegeman and Englis (22).

*The Oxidation of Organic Compounds Using Perchloric Acid Solutions of the Perchlorato-Cerate Ion.*—The inconvenience of the use of alkaline permanganate in the determination of organic compounds and the empiricism of the ceric sulfate procedure of Willard and Young make it desirable to seek another procedure. If the procedure can be made to combine the simplicity of the latter system with the general applicability of the former and, at the same time, involve none of the empiricism of the latter method, the development may be said to be a distinct advantage. Such a procedure has been developed through the simple expedient of the substitution of perchloric acid solutions of  $\text{Ce}(\text{ClO}_4)_6$ — as the oxidant. The higher potentials of the cerate systems in perchloric acid solution as compared to the sulfato-cerate system in sulfuric acid medium, together with a definite specificity of reaction not provided by use of the Willard and Young procedure (20), account for the generally improved conditions. The reaction mechanism can be definitely stated and as a result of the fact that the oxidation equivalents involved are the theoretical ones, the reaction products are definitely known. Polyhydric alcohols, pentoses, hexoses, and invert sugars

are included as well as organic acids and other oxidizable products. The time factor for oxidation with the excess cerate ion is lowered, and the temperature at which comparatively rapid oxidation occurs is likewise decreased. Reaction products are formic acid or  $\text{CO}_2$  or both, and sometimes acetic acid is produced. The conditions for the new procedure are in general as follows: A solution of the organic compound in 4 M perchloric acid is oxidized by an excess of a standard solution of  $\text{Ce}(\text{ClO}_4)_6^{4-}$  or  $\text{Ce}(\text{NO}_3)_6^{4-}$  in 4 molar perchloric acid. The reaction is allowed to take place at room temperature, or at slightly elevated temperature (45 to 60 C.), for 10 to 30 min. The excess of cerate ion is then determined by titration with standard oxalate solution, using nitro-ferroin (or ferroin) as indicator. The first formation of a pink solution indicates the completion of the reaction with excess cerate ion.

The best method for the determination of cerous cerium is that of Willard and Young (23). The use of the nitrato-cerate ion in nitric acid solution as a reagent in qualitative organic identifications and its application to the detection of alcoholic hydroxyl groups have been described by Smith and Duke (24).

*Summary of the Most Important Determinations Involving the Use of Tetravalent Cerium in Volumetric Analysis.*—The elements that have been determined by the use of tetravalent cerium solutions are shown in Table V. For this purpose the scheme introduced by Lundell and Hoffman (25) was used. The elements enclosed in solid lines are determined by a direct procedure while those enclosed by dotted lines are determined by an indirect titration. Other elements of Table V might well be determined, for example, titanium. All the elements thus determined are included in the group most frequently called for in applied chemical analysis. The references to the literature describing the determinations indicated are all given in the review paper by Furman (4).

TABLE V.—ELEMENTS DETERMINED BY PROCEDURES INVOLVING OXIDATION WITH TETRAVALENT CERIUM<sup>a</sup>

<sup>a</sup> Elements enclosed in solid lines are determined by direct titration. Elements enclosed in dotted lines are determined by using an indirect procedure.

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## Micro-Gas Analysis Methods and Their Application to Research

By L. A. Wooten<sup>1</sup>

**T**HE ANALYSIS of minute quantities of gases has been accomplished by application of conventional high-vacuum techniques developed primarily in connection with investigations of electron emission and the development of vacuum devices. The low-pressure method of micro-gas analysis based upon these techniques was first employed by Langmuir (1)<sup>2</sup> in 1912 in the course of his classic investigations of reactions occurring between certain gases and a heated tungsten filament. Since that time the method has found many applications to research and has become an invaluable analytical tool. Ryder (2) in 1918 published an improved form of apparatus and applied it to the analysis of gases evolved from metals when heated in vacuum. Norton and Marshall (3) and Smithells and Ransley (4) have applied the method to studies of gases in metals. Dalton (5) has analyzed gases evolved from glass. Specialized forms of apparatus have been developed for the analysis of the oxygen and nitrogen content of metals by the vacuum-fusion process developed by Jordan, Oberhoffer, and others. A typical apparatus for application of the vacuum-fusion process has been described by Chipman and Fontana (6). A review of the methods for the determination of gases in metals and results obtainable is found in a paper by Thompson, Vacher, and Bright (7).

Prescott and Morrison (8) have described new forms of apparatus for general microanalysis of gases by the Langmuir method and have applied the method to the determination of the free alkaline earth metal content of the oxide coated cathode. Methods were developed by these workers for gas mixtures of water vapor, carbon dioxide, hydrogen, carbon monoxide, and oxygen or methane. The apparatus described is shown to be applicable to samples of 1 cu. mm. to 25 cu. mm. with a precision of

measurement of plus or minus 5 per cent or better on the basis of the total sample. The limit of sensitivity is 0.02 cu. mm.

Another development of importance in the field of micro-gas analysis was that of Campbell (9) who proposed a procedure which depends upon the characteristic form of vapor pressure-temperature curves. In this method, gases condensable in a trap at liquid nitrogen temperature are fractionated by a low-temperature distillation and identified by the temperature range, characteristic of each gas present, over which a rapid rise in pressure occurs. (The temperature at which a pressure rise is detected is limited, of course, by the sensitivity of the pressure gage.) Mixtures of gases consisting of several components may be analyzed by this method, provided the apparatus is calibrated by running mixtures of known composition. Sebastian and Howard (10) have applied the method successfully to the analysis of mixtures of hydrocarbon gases, and similar applications have been made in the author's laboratory. The low-temperature distillation method is uniquely applicable to mixtures of condensable gases that are mutually reactive, such as sulfur and oxygen compounds. Frequently this method, as will be shown in a following section, can effectively be employed to separate gases in the condensable fraction of a mixture, preliminary to their identification by the use of chemical reagents. The method fails, of course, on mixtures which form solid solutions in the condensed phase.

Although this paper will be concerned only with applications of the low-pressure method, mention should be made of the constant-pressure methods of micro-gas analysis such as those described by Blacet and Leighton (11), and Sutton (12). These methods, under the best conditions, require 100 cu. mm. of gas, which can be analyzed with a precision of plus or minus 0.2 per cent, while a complete analysis on a fairly complex sample may be made on 1 cu. mm. by the low-pressure method.

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<sup>2</sup> The italic numbers in parentheses refer to the reports and papers appearing in the list of references appended to this paper.

## GENERAL TECHNIQUES

In the low-pressure method of gas analysis the gases are circulated and collected by means of Toepler pumps, confined by mercury cutoffs, and finally measured in a capillary burette or in a calibrated volume by a McLeod gage. In making an analysis, the gas mixture is circulated over specific reagents or through freezing traps, held at appropriate temperatures, to remove each constituent one by one, the resulting pressure changes being measured in a standard volume. In certain cases the time of analysis may be greatly reduced by the use of a miniature mercury diffusion pump in series with the Toepler pump (3, 8). The operation of the Toepler pump may be made automatic by application of a simple electron-tube circuit.

**Pressure Measurement.**—Although many devices have been developed for the measurement of low pressures, the McLeod gage is the most widely used in micro-gas analysis. If not used directly, it must be employed as a means of calibrating the working gage, owing to the fact that throughout the range of pressures in which we are interested no other absolute gage possesses comparable accuracy. The chief limitations of the McLeod gage have resulted from the tendency of mercury to stick to the walls in small glass capillaries, thus making it necessary to work with 1-mm. bore or larger. Rosenberg (13) has recently reported that grinding the inner surface of capillary tubing greatly diminishes the sticking of mercury in the operation of a McLeod gage. Tests in the author's laboratory of a gage constructed of 0.7-mm. bore tubing, ground according to Rosenberg's method, show virtually no sticking. Cleanliness is important, but certainly no more so than with smooth capillaries. Thus this technique increases by large factors both the sensitivity and accuracy of low-pressure measurements.

**Introduction of Gases into Vacuum Systems.**—In gas reaction studies and in gas analysis it is frequently necessary to introduce a small quantity of a pure gas into a vacuum or low-pressure system. This may conveniently be accomplished by the scheme shown in Fig. 1 (*D*). Porous lavite plugs, sealed into glass tubes, when brought together under mercury, allow gas to pass from vessel *B* to the system marked *C*. By varying the porosity or length of the plug, the rate of diffusion of gas can be controlled.

Another method of introducing pure gases is by the use of metallic semipermeable membranes, several of which are specific. It has long been known that hydrogen will diffuse through palladium at elevated temperatures. The device shown in Fig. 1 (*E*) makes use of this property of palladium as a means for the introduction of hydrogen into a vacuum system.

The device consists of a palladium tube closed at one end and soldered to a platinum tube at the other, which is in turn sealed into a glass tube. The temperature of the palladium tube is regulated by means of a heater wound on the palladium tube but insulated from it by asbestos cement. This scheme insures the purity of the hydrogen as well as providing a means of introducing the gas at a steady, easily controllable rate. Silver has been employed by J. B. Taylor (14) as a semipermeable membrane for the introduction of oxygen into low-pressure systems. In the use of silver it is important that the membrane be protected from mercury vapor. Other metal-gas diffusion systems are described by Jossem (15) who gives data on the calculated rates of diffusion for various systems.

A method for opening a sealed tube under vacuum has been described by Brady (16). In this method a heated tungsten probe is used to puncture the glass wall of the tube to be opened. The tube containing the tungsten probe is attached to the glass wall by means of a wax seal, thus enclosing the area to be punctured.

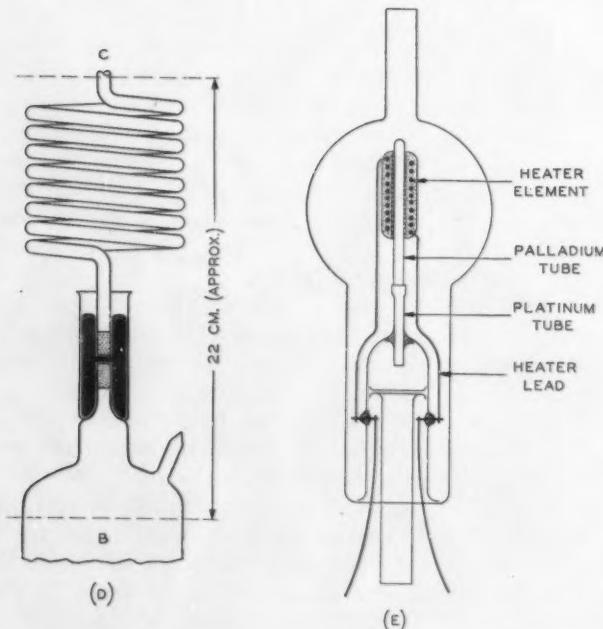


Fig. 1.—Apparatus for the Introduction of Pure Gases into Low-Pressure Systems.

*D*—Porous lavite plug system.  
*E*—Metal-gas diffusion valve.

## APPLICATIONS

The high sensitivity of low-pressure gas analysis methods makes them especially suitable for studying reactions occurring in gases or between a solid and a gas at low pressures. The methods are also applicable to the analysis of thin films where the films can be converted to a gas by a simple quantitative reaction with a suitable reagent. The following applications of micro-gas analysis methods have been selected with a view to showing the versatility of these methods as applied to research and analysis. The experimental methods to be described are extremely simple in principle and for the most part require simple and inexpensive apparatus.

### 1. Analysis of Tarnish Films on Metals (16a):

The composition of surface films which form upon exposure of silver and copper to natural or synthetic atmospheres may be deduced from information obtainable by micro-gas analysis, provided the films are of a simple type. The method consists of reducing the tarnish film with a suitable reagent and of identifying the reaction product by means of the low-temperature fractionation method, supplemented by chemical tests. Having identified the surface compound, the thickness of the film may be computed from the quantity of the reduction product and the area of the specimen (assuming the density of the surface

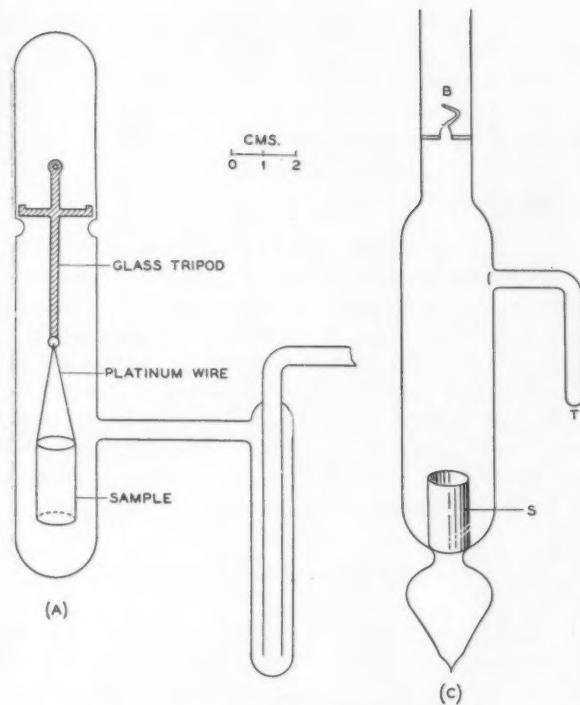


Fig. 2.—Apparatus for the Analysis of Tarnish Films on Metals.

compound is the same as that of the pure compound in bulk).

The specimen to be analyzed in cylindrical form is suspended coaxially in a vertical tube as shown in Fig. 2 (A). The reagent gas (either hydrogen or carbon monoxide) is introduced into the system by one of the methods previously described. The sample is heated by high-frequency induced current with the trap surrounded by a liquid nitrogen bath. The reduction products are thus condensed in the trap as rapidly as formed and the surface reaction goes quickly to completion at low temperature. The excess reagent is pumped from the system and the reduction products are distilled into a second trap ( $T_3$ , Fig. 3) which is surrounded by the special Dewar flask for obtaining the vapor pressure-temperature curve. The function of the special flask is to permit close control of the rate of increase of temperature of  $T_3$ . Figure 3 shows the details of this arrangement.

Hydrogen is the most suitable reagent for films on silver which are usually composed of silver sulfide. Carbon monoxide was selected as the most suitable reagent for films on copper, because the films with which we worked were found to be mainly cuprous oxide.

Since hydrogen sulfide and carbon dioxide give similar vapor pressure-temperature curves, it was necessary to devise a test for differentiating between the two gases. This was done by passing the gas, after tentatively identifying it by the characteristic vapor pressure curve as either hydrogen sulfide or carbon dioxide, over silver oxide at approximately 100°C. If the gas is hydrogen sulfide, it reacts with silver oxide to form silver sulfide with the evolution of water vapor. If the gas is carbon dioxide, no reaction occurs at this temperature. The side arm in Fig. 3 shows the schematic arrangement of apparatus for the identification of the hydrogen sulfide.

When the first component has evaporated, the mercury cutoff is lowered and the gas is condensed in trap  $T_1$ . The cutoff is raised and the vapor pressure curve continued if other components are expected to be present.  $R$  is a silver surface on which has been deposited a layer of active silver oxide by low-pressure discharge in oxygen. The hydrogen sulfide is circulated over this silver surface at approximately 100°C. by distilling from  $T_1$  to  $T_2$  and back to  $T_1$ . Complete reaction occurs in two or three passes.

Figure 4 shows the vapor pressure curves of the condensable reduction products obtained on reducing tarnish films on three silver specimens with hydrogen. Curve No. 1 was obtained on a silver specimen exposed to synthetic atmosphere containing hydrogen sulfide. The sulfur computed from this analysis in micrograms per square centimeter was 10.8 as compared with 11.1 obtained by the weight gain method. Curves Nos. 2 and 3 were silver specimens exposed 81 and 28 days, respectively, to an indoor city atmosphere. The main component was proven to be hydrogen sulfide, and from this we concluded that the film is composed principally of silver sulfide. In addition to hydrogen sulfide, curve 2 shows the presence of traces of two unidentified gases, possibly carbon disulfide and water vapor.

Films formed on exposure of copper to indoor city atmospheres have also been analyzed by this method.

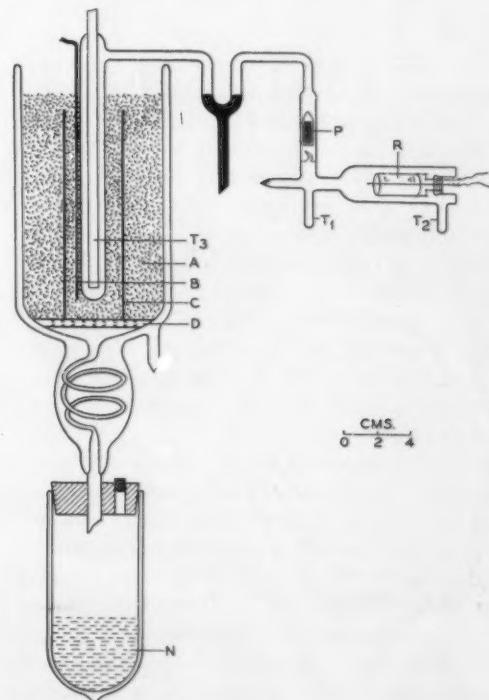


Fig. 3.—Apparatus for the Analysis of Gas by Low-Temperature Fractionation.

- A—Copper turnings.
- B—Copper-constantan thermocouple.
- C—Copper shield.
- D—Perforated porcelain plate.
- N—Liquid nitrogen.
- $T_1$ —Copper jacketed freezing trap.
- P—Magnetic hammer.

$T_1$  and  $T_2$ —Freezing traps.  
 $R$ —Reagent for chemical identification of a gas.

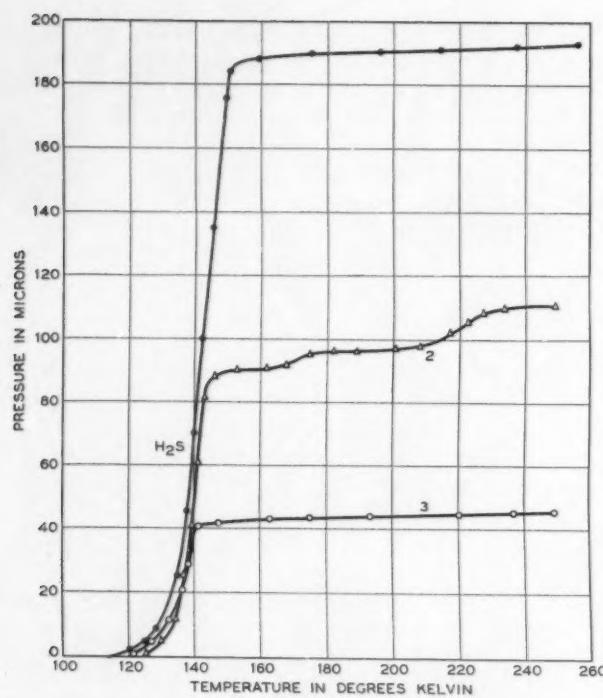


Fig. 4.—Vapor Pressure Curves of Reduction Products of Films on Silver.

1. Silver exposed to a synthetic atmosphere containing hydrogen sulfide.
2. Silver exposed 81 days to an indoor city atmosphere.
3. Silver exposed 28 days to the same atmosphere as 2.

These films were found to consist mainly of cuprous oxide mixed with a carbonaceous material. It was found that on reduction with carbon monoxide, the product obtained was carbon dioxide. On heating in vacuum, the copper oxide films were also completely reduced giving carbon dioxide and carbon monoxide, which indicates the presence of a carbonaceous material.

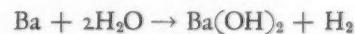
The chief problem encountered in applying the method to naturally formed films is the complication due to the evolution of gases from the metal itself. Errors due to this source were minimized by the use of pure oxygen-free metal specimens and by heating the specimen for the minimum time and at the minimum temperature required to reduce the film.

The method is much more suitable to the study of tarnish reactions in a controlled system using synthetic atmospheres. We have made preliminary studies on both silver and copper, using oxygen and mixtures of sulfur gases and oxygen. In Fig. 2 (C) is shown schematically the very simple apparatus used in carrying out these studies. An outline of the procedure is as follows: The apparatus with the sample enclosed is sealed to the pump station, evacuated, and out-gassed. Hydrogen is then introduced into the system and the metal specimen heated to reduce any surface film already present. After again evacuating, the gas mixture to be studied is introduced into the system, the condensable fraction of this gas is condensed in the trap  $T_1$ , and the apparatus is sealed off. The reactions are either allowed to proceed at room temperature or the entire apparatus is thermostated at the desired temperature. At the end of the reaction period, the apparatus is sealed to the gas analysis system and, after out-gassing and conditioning the system, the breakable

tip at  $B$  is broken by means of a magnetically operated weight. The residual gases from the tarnish reactions are then analyzed and a suitable reagent is introduced for analysis of the surface film. The mechanism of certain tarnish reactions may thus be investigated.

## 2. Analysis of Thin Metal Films:

The determination of the free metal content of electron-emitting surfaces of the composite type has been of considerable interest in studies of electron emission. Analyses of this type have been accomplished by employing as a reagent a gas that will oxidize the free metal quantitatively and give an equivalent of an easily measured gas. Both water vapor (17) and carbon dioxide (18) have been applied to the determination of the free metal content of thermionically active alkaline earth oxide cathodes. In the water vapor method the reaction



occurs at room temperature giving one mole of hydrogen for each mole of free barium present. Carbon dioxide will oxidize barium at 900 C., giving carbon monoxide as a reduction product (18).

The water vapor method is generally applicable to the determination of microgram quantities of the alkali and alkaline earth metals and certain other metals such as aluminum. The method is being employed in the author's laboratory to study rates of reaction between metals and metal oxides at high temperature in vacuum in cases where a volatile metal is formed by reduction and evaporates to a cooler portion of the system. Lederer (19) used the water vapor method in studying the production of free

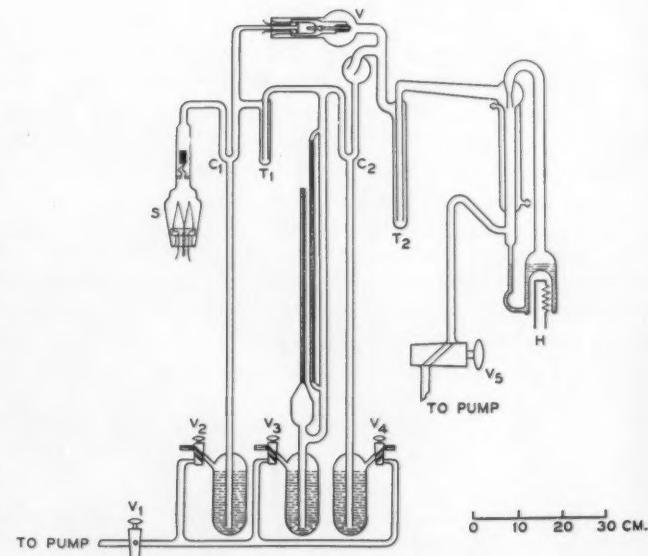


Fig. 5.—Apparatus for the Analysis of Thin Metal Films by the Water Vapor Method.

- S—Reaction tube.
- V—Palladium valve.
- $C_1$  and  $C_2$ —Mercury cutoff.
- $T_1$  and  $T_2$ —Freezing traps.
- $V_1$ ,  $V_2$ ,  $V_3$ ,  $V_4$ , and  $V_5$ —Stopcocks.
- H—Heater for diffusion pump.

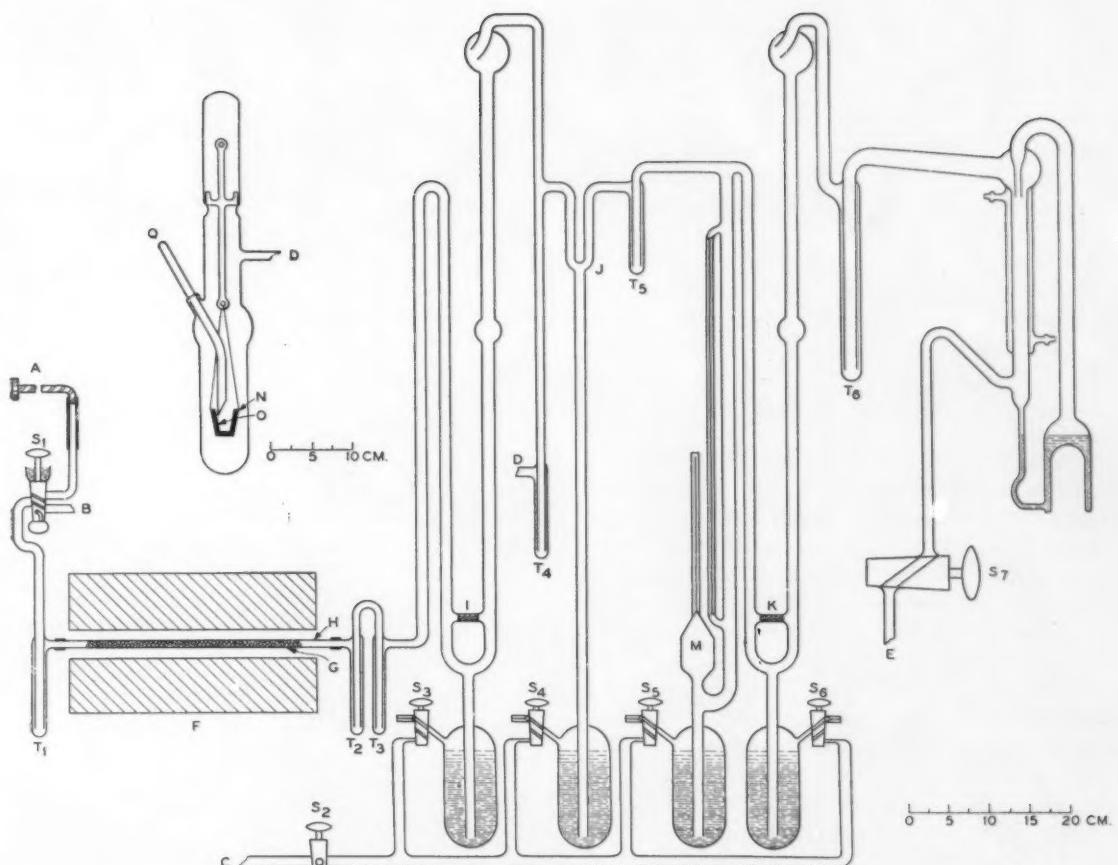


Fig. 6.—Apparatus for the Determination of Carbon by the Low-Pressure Combustion Method.

- A*—Flexible copper tube with copper-to-glass seal.
- B* and *C*—Outlets to oil pump.
- E*—Outlet to oil pump.
- T<sub>1</sub>*—*T<sub>6</sub>*—Traps.
- F*—Electric furnace.
- G*—Palladium catalyst on asbestos.
- H*—Clear quartz tube.
- I*, *J*, *K*—Mercury cutoffs.
- M*—McLeod gage.
- S<sub>1</sub>*—*S<sub>7</sub>*—Stopcocks.
- N*—Platinum crucible.
- O*—Magnesia crucible.

barium by the reaction of barium berylliate with tantalum at 1100 to 1200 C.

An apparatus for the general application of the water vapor method is shown in Fig. 5. The sample tube containing the reactants in the form of a filament is designated as *S*. Water vapor is purified by distillation and is introduced into the system and held in a low-temperature trap. By means of a breakable glass tip, the water vapor is introduced into the reaction tube. When the reaction is complete, the excess water vapor is recondensed and the pressure of the noncondensable gas obtained from the reaction is measured. The heater on the palladium valve is now turned on and the gas, if hydrogen, rapidly escapes from the system. A second pressure measurement is made to detect any residual gas, not hydrogen. If the quantity of hydrogen is small it may be collected (by means of a Toeppler pump) in a capillary burette for final measurement.

### 3. Determination of Carbon in Low-Carbon Iron and Iron Alloys:

The determination of carbon in low-carbon iron and steel presents difficulties not easily overcome by the conventional carbon combustion method. The low-pressure combustion method applied to the problem has been developed into a high precision method (20).

The method developed consists of the combustion of the sample in an all-glass apparatus, the collection of the carbon dioxide by condensation in a liquid nitrogen trap, and, after pumping out the excess oxygen, the determination of the carbon dioxide by a vapor pressure measurement in a standard volume. The sample, contained in a ceramic crucible, which is fitted into a platinum crucible, is heated by means of a high-frequency induction furnace, the outside platinum crucible serving as a heating element.

Yensen (21) and Ziegler (22) have described somewhat similar methods for the determination of carbon by the

vapor pressure method, but they did not employ high-frequency heating, hence could not use an all-glass system.

The apparatus developed for the determination of carbon is shown in Fig. 6. It consists essentially of a purification system, a combustion chamber, and an analysis system, connected to a mercury diffusion pump backed by an oil pump. The oxygen, admitted at *A* through a flexible copper tubing, first passes through a liquid nitrogen trap, then over a palladium catalyst at 1000 C., and finally through two more traps at liquid nitrogen temperature before being admitted to the combustion chamber. The capillary by-pass in cutoff *I* is a device for admitting oxygen at a relatively high pressure of about 16 cm. to the evacuated system. The capillary at *K* serves a similar purpose in exhausting the excess oxygen. *M* is a McLeod gage. The combustion chamber is sealed on at *D* and is shown in detail in the upper left of Fig. 6. It consists of an E. J. Pyrex glass tube in which is suspended coaxially a platinum crucible which contains the refractory crucible. The sample, in the form of millings or thin turnings, is introduced into the refractory crucible *O* through the side tube *Q*. The platinum crucible is of standard form with reinforced rim of approximately 15-ml. capacity. The refractory crucible used is an alumina or magnesia crucible supplied by Norton Co. The blank on this crucible is readily reduced to a very low constant value by prefiring in oxygen.

The oxygen is purified by liquefying approximately 10 ml. in trap *T*<sub>1</sub> and then evaporating a portion of this and recondensing it in traps *T*<sub>2</sub> and *T*<sub>3</sub>. These traps collect any oxidation products formed by passing the oxygen over the palladium catalyst, and they also hold the liquid oxygen until ready to be admitted to the system. At liquid nitrogen temperature the vapor pressure of oxygen is approximately 16 cm., so that it is possible to hold a supply of pure oxygen in trap *T*<sub>3</sub> while evacuating and outgassing the analysis and combustion systems. The mercury cutoff at *I* is employed as a manometer. An analysis is run as follows: Cutoff *K* is raised and cutoff *I* is lowered

by manipulating stopcocks *3* and *6*, allowing the oxygen at first to pass through the capillary at *I* and bubble up through the mercury column. After the pressure in the purification and analysis system has equalized, cutoff *I* is closed and the platinum crucible heated by high-frequency induced current to a temperature of 1100 C. Heating is continued for 15 to 20 min. to insure complete combustion. Prior to burning the sample, a liquid nitrogen bath is placed on trap *T*<sub>5</sub> and a dry ice-acetone bath on trap *T*<sub>4</sub>. The carbon dioxide obtained is condensed in trap *T*<sub>5</sub>, the excess oxygen is pumped from the system, and the cutoff *J* is raised. The carbon dioxide is then allowed to evaporate and attain thermal equilibrium, and a vapor pressure measurement is made. Knowing the volume of the system and the vapor pressure, the carbon content of the sample is computed.

The precision of this method has been found to be plus or minus 10 per cent on samples containing 0.001 per cent carbon. The method is applicable not only to low-carbon iron and iron alloys but also to higher carbon samples where only a very limited sample is available. For example, the method has been applied to the determination of carbon in samples of vacuum tube filament core materials weighing only a few milligrams.

#### SUMMARY

The application of modern high-vacuum techniques to analysis and research has been of particular value in the study of gas-metal equilibria, such as are involved in adsorption, diffusion, and solubility of gases in metals, and in studies of the composition of electron emitting surfaces. The high sensitivity and easy adaptability of low-pressure methods make them especially suitable for studying reactions occurring in gases or between a solid and a gas at low pressures. The methods are also applicable to the analysis of very thin films where the film to be analyzed can be converted to a gas by a quantitative reaction with a suitable reagent.

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## Technical Publications Issued

OF THE SPECIAL TECHNICAL publications recently issued by the Society several are special compilations of standards. The 1940 publication schedule provided for the issuing of nine of these compilations, each of which gives in convenient, compact form all of the Society's specifications, tests, definitions, and recommended practices for the specific fields covered. Some of the books include other pertinent material covering such things as abstracts of papers, special reports, draft standards, and the like.

Early in December the compilation covering electrical insulating materials became available, giving in addition to some 45 specifications and tests several special reports dealing with the significance of various tests. This 340-page publication also included the latest report of Committee D-9, which gives in detail changes in specifications and tests.

Under the sponsorship of Committee D-5 on Coal and Coke, there have been issued at various intervals compilations of standards in this field. The last one published was in 1938 and the 1940-1941 edition includes a number of changes made in the interval. This publication of 160 pages includes the personnel of the committee and all the definitions, tests, specifications, as well as the widely used methods of sampling and laboratory analysis of coal and coke.

Most recent of the compilations are those covering the field of refractory materials and rubber products, each of these having just come off press. Each has been considerably expanded over the previous edition and provides much information and data, in addition to the A.S.T.M. standards. This is particularly true of the refractories manual which includes nine rather extensive surveys of service conditions for the use of refractories in various industries. In addition there is information on standard samples of refractory materials and other data.

The volume sponsored by Committee D-11 on Rubber Products has been enlarged by several new standards, a number of the existing ones were changed and there is a valuable bibliography which provides a listing of the more important references in the field covered.

The ninth compilation, to be issued about January 25, is one of the most extensive ones, giving over 100 tests, definitions, and specifications covering paints, varnish, lacquer, and related materials developed through the work of Committee D-1. It is greatly changed as compared with the 1935 edition and should be of much value to paint technologists, chemists, and others concerned with not only the production but the use of the materials.

### 1940 Proceedings Aggregate 1400 Pages

THE DISTRIBUTION beginning on January 30 of the 1940 *Proceedings* of the Forty-third Annual Meeting marks the completion of another of our major publications. This volume of 1400 pages, now issued in one part, comprises first, the technical committee reports and, second, the technical papers. If anyone wishes a complete picture of the Society's work during the year covered in both the fields of standardization and research, the *Proceedings* is the one place where it can be obtained.

SPECIAL COMPILATIONS COVERING:	MEMBERS PRICES	LIST PRICES
Steel Piping Materials for High Temperature (wire ring binder).....	\$1.00	\$1.25
C-1 on Cement.....	0.75	1.00
C-8 Refractories Manual: Wire ring binder.....	1.15	1.50
Cloth binding.....	1.40	1.75
D-2 Petroleum Products.....	1.50	2.00
D-5 Coal and Coke.....	1.00	1.25
D-9 Electrical Insulation.....	1.50	2.00
D-11 Rubber Products.....	1.25	1.75
D-13 Textile Materials.....	1.25	2.00
D-1 Paints.....	1.50	2.00

The committee reports cover the detailed work of each of the some 60 standing committees. Most of these reports are preprinted in advance of the annual meeting in order that considered action can be taken on the various standards recommendations. While an earnest effort is made to preprint the technical papers to be presented at the meeting, this year for a number of reasons, some could not be set in type prior to the meeting, although abstracts were made available. Consequently, the members will be interested in reviewing the papers in the *Proceedings*, some of them being quite extensive, and all, important technical contributions.

In addition to itemized actions on standards many of the committee reports include results of research investigations, some of which form the basis of standardization actions; others are involved with developing knowledge of the properties of materials not essentially for specification work.

The section of the *Proceedings* devoted to technical papers constitutes the major portion of the volume and the opening item is of widespread interest since it is the Edgar Marburg Lecture by P. H. Bates, covering portland cement. A Symposium on Significance of the Tension Test of Metals in Relation to Design covering some 110 pages with four separate papers occupies an important place. There are other contributions on ferrous and non-ferrous metals. Various topics in fields of cement, concrete, and masonry materials are covered in a series of papers and the Symposium on Problems in the Classification of Natural Water Intended for Industrial Use is one of another important group of technical papers, covering some 50 pages.

Two outstanding papers in the plastics field, one covering the accelerated weathering of transparent plastics and the other covering sorption of water by plastics were not preprinted.

Also worthy of note is the amount of discussion which the technical papers elicited; in particular the discussion of the Symposium on Tension Testing, joint discussion on bursting tests of lead sheathings, and joint discussion on effect of speed of testing.

The publication is complete with a detailed subject and author index. Each member of the Society receives a cloth-bound copy of this book. Copies are also procurable in half-leather binding at the extra cost of \$1.00. Extra copies in cloth binding can be purchased by members for \$6.00; the list price to nonmembers is \$9.00 per copy.



JANUARY 1941

# Bulletin

TWO-SIXTY  
SOUTH BROAD ST.  
PHILADELPHIA, PENNA.

NO. 108

## Importance of District Meetings

THE IMPORTANCE and value of meetings of the Society sponsored by various District Committees in leading industrial centers has been stressed. In this BULLETIN there are announcements of the forthcoming Cleveland, and Southern California meetings, and sessions are also contemplated in Pittsburgh, Detroit, and New York. The Executive Committee of the Society, when it established the present District Committee organization several years ago, was fully cognizant of the fact that to attempt to superimpose monthly meetings in the Society districts on an already over-burdened schedule of meetings of other local and sectional groups would be unwise, but that a policy of holding one or two outstanding meetings a year would be sound.

Many of the meetings held have been outstanding, a number of valuable publications have resulted and in every instance the papers and addresses given have been worth while and have evoked much interest.

Fundamentally, District Committees are responsible for stimulating and maintaining interest in the work of the Society in their particular area. Meetings are one means of accomplishing this purpose. Not only are they valuable in promoting knowledge of A.S.T.M. work in standardization and research among the individuals, companies, and industries in an area, but they also serve to knit more closely the A.S.T.M. members and committee members in these districts. With at most two meetings a year to support, the district officers look to, and have very generally received, the interest of all A.S.T.M. members in their area. The district meeting affords a fine opportunity to meet fellow members and the district officers and Society officers who are usually present, and basically to broaden one's knowledge of some pertinent subject in the field of materials.

These meetings at the present time are of particular import because a number are focusing attention on the importance of specifications work in connection with industrial problems as related to National Defense.

## Last Call for Meeting Papers

DETAILED CONSIDERATION will be given to the program for the 1941 Annual Meeting to be held at The Palmer House in Chicago, June 23-27, by Committee E-6 on Papers and Publications at its meeting about the middle

of February. At this time offers of papers for presentation at the annual meeting will be studied from the standpoint of importance, nature of the particular problem involved, and also its relation to other topics on the program.

While a number of offers have already been received, there are undoubtedly still a number of individuals who may have papers in course of development, or under consideration, and who may wish to transmit offers. These should be received at A.S.T.M. Headquarters not later than February 1; blanks to be used in transmitting the information can be obtained on request.

Recently comments have appeared in the technical and business press concerning what effect the present intensive industrial activity brought about by National Defense efforts may have on the ability of men in industry to prepare technical papers and reports. Apparently, during the last war, there was a very abrupt falling off in the number of well-prepared technical contributions, perhaps traceable to a slackening in research activities. Responsible Government officials as well as editorial comment have emphasized the necessity of keeping research on the forward march. From the Society's standpoint, and consequently of industry's, too much stress cannot be laid on the importance of a continuous flow of data and information on the properties and tests of materials, much of which must take the form of technical papers.

## Members: Be Sure to File Your Index

WHILE REFERENCE was made in the December ASTM BULLETIN to the importance of the latest *Index to Standards*, as of December, 1940, attention is again directed to this publication. A copy was mailed to each member about the middle of December and each purchaser of any part of the Book of A.S.T.M. Standards or 1940 Supplements also received a copy. This latest Index is of outstanding importance because it takes the place of a subject index which might otherwise be published in each part of the Supplement to the 1939 Book of Standards. It was felt to be more desirable to have one complete Index available, which accounts for the note in each of the Supplements that the Index to A.S.T.M. Standards should be used in lieu of an index to each part. Consequently, this publication should be filed with the Book of Standards because in one sense it is an inherent part of this publication. Extra copies will be furnished to anyone having use for them.

In addition to its utility in facilitating the use of the Book of Standards and the Supplements, it is the only place where there is published a complete list of A.S.T.M. standards in numeric sequence. Furthermore, it is the only source where a member or others concerned with specifications or tests can determine quickly by the carefully selected headings under which standards are listed whether or not A.S.T.M. has issued a specification or method of test on a particular subject or material.

If those using the Book of Standards will keep the Index handy and use it there should be no difficulty whatsoever in locating a standard in the latest publication where it appears; also in determining what is the latest standard; and finally, as mentioned above, whether or not there is a standard on a particular subject.

SO KEEP THE INDEX ON FILE!

## **Eighteen New Sustaining Members as of January 1**

**A**S OF JANUARY 1, 1941, 18 companies, each previously connected with the Society, have become Sustaining Members. With this very encouraging increase, the number of Sustaining Members has now reached a total of 126. One of the notable developments during 1940 in connection with support of the Society through membership has been the large number of companies who have been willing to subscribe to this class.

From the accompanying condensed information it will be noted that in practically all cases the companies are quite active in many phases of A.S.T.M. work and are actively supporting many different projects.

Some of the distinct advantages of Sustaining Membership have been enumerated. First, the receipt of a copy of every publication issued by the Society which includes

quite a number ordinarily furnished only on purchase. There is no extra charge to Sustaining Members for a complete set of the Book of Standards, and further, an extra complete set is furnished on request. Also, extra copies of the ASTM BULLETIN can be procured by Sustaining Members for distribution to their executives and engineers who are following A.S.T.M. work.

The Society is very appreciative of the cooperation of these companies in rendering increased financial support. For individual membership, which applies also to government departments, universities, libraries, and the like, the regular dues are \$15. Company or corporate members pay \$30 dues yearly. This applies to firms, corporations, laboratories, and associations. Sustaining Members, who may be individuals, companies, or corporations, contribute \$100 annual dues.

### **New Sustaining Members**

**NATIONAL GYPSUM CO., D. D. CRANDELL, DIRECTOR OF RESEARCH, BUFFALO, N. Y.**

Actively engaged in various phases of the work of the Society since 1929, which is the date the membership held by this company became effective, this organization since it acquired membership has been represented by Mr. Crandell. During this time he has been a member of Committee C-11 on Gypsum, serving on three of its subcommittees dealing with gypsum plasters, structural products, and testing methods. C. J. Koehler represents the company on Committee C-7 on Lime, serving on Subcommittee V on Methods of Test for Lime and Lime Products.

**LACLEDE STEEL CO., W. W. SCOTT, JR., VICE-PRESIDENT, ST. LOUIS, MO.**

Active supporters of the Society through various memberships, this company has been affiliated with A.S.T.M. since 1912 which was the date the membership of Thomas R. Akin, President, then and now, of the company, became effective. Later this was transferred to a company membership. In 1923 another company membership was taken out with Mr. Scott as the official representative. W. W. Arpe, Assistant General Manager of Sales, has been a personal member of the Society for some 15 years. With respect to committee activities, Mr. Scott has served on Committee A-1 on Steel since 1924. He is a former member of the St. Louis District Committee.

**RIVERTON LIME AND STONE CO., INC., WILLIAM E. CARSON, PRESIDENT, RIVERTON, VA.**

Affiliated with the Society since 1920, first, through a membership held personally by Mr. Carson which was later transferred to a company membership, this organization is particularly interested in the work of three standing committees, C-1 on Cement, C-7 on Lime, and C-12 on Mortars for Unit Masonry. Mr. Carson has served for some ten years on C-1. On Committee C-7, P. L. Rogers serves with Mr. Carson, while on Committee C-12 Mr. Rogers serves as the representative. Mr. Carson has served on a number of subcommittees of C-7 and C-12 and has been chairman of several of them. At present he is chairman of Subcommittee X on Hydraulic Lime of C-7.

**ALEXANDER SMITH AND SONS CARPET CO., A. GRIFFIN ASHCROFT, PRODUCT ENGINEER, YONKERS, N. Y.**

Mr. Ashcroft's connection with the Society dates from 1933. Two years later the company became members of the A.S.T.M. with Mr. Ashcroft being designated as the representative. He has been extremely active, in particular, on Committee D-13 on Textile Materials on which he has been a member since 1933. He is chairman of D-13's Subcommittee A-3 on Wool and its Products and of Subcommittee B-5 on Sampling Presentation and Interpretation of Data. He is also an active member of

other groups including those on bast and leaf fibers and their products, household and garment fabrics, and represents the textile committee on Technical Committee XI of E-1 concerned with designation and interpretation of numerical requirements. He also represents his company on Committee D-12 on Soaps and Other Detergents. He is a representative of the Society on the Joint Committee for the Development of Statistical Applications in Engineering and Manufacturing and serves on the Inter-Society Color Council. Oliver Beckwith is also active in committee work on behalf of his company, serving on several subcommittees of the textile group.

**UNITED ENGINEERING AND FOUNDRY CO., H. H. TALBOT, SENIOR ENGINEER, PITTSBURGH, PA.**

Although this organization did not officially become company members of the Society until 1937, Harry E. Walters metallurgist of the company for many years, now retired, has been a member of the Society continuously since 1908. F. H. Allison, Jr., Metallurgist at Vandergrift, Pa., has been a personal member for a number of years. Mr. Allison is a member of Committee A-1 on Steel, serving on its subcommittees on forgings and castings. The company is represented on Committee A-3 on Cast Iron by S. L. Feduska.

**THE UDYLITE CORP., GUSTAF SODERBERG, TECHNICAL DIRECTOR, DETROIT, MICH.**

This company actively represented on a number of standing committees has been affiliated as a company with the Society since 1929, Mr. Soderberg having served as representative of the company for a number of years. He is actively concerned with two of the Society groups functioning in the fields of corrosion; namely, Committees A-5 on Corrosion of Iron and Steel and B-3 on Corrosion of Non-Ferrous Metals and Alloys. On the former he is a member of three subcommittees while on B-3 he is on four of its subcommittees. He also serves on the subcommittee on finishing properties of Committee B-6 on Die-Cast Metals and Alloys. His activities on Committee A-5 have extended over ten years.

**UNITED STATES PIPE AND FOUNDRY CO., ARTHUR E. SCHUH, DIRECTOR OF RESEARCH, BURLINGTON, N. J.**

1941 will be the thirty-third year that this company has been affiliated with this Society, its membership dating from 1908. Mr. N. F. S. Russell, President, has been interested in Society work for many years. He formerly represented the American Foundrymen's Association on Committee A-3 on Cast Iron and has taken a leading part in the work of Sectional Committee A-21 on Specifications for Cast-Iron Pipe and Fittings. Mr. Schuh became representative for the company when he was appointed Director of Research in 1938. H. W. Stuart, Assistant Director

of Research, has been for many years active in the work of Committee A-3 and at present serves on four of its subcommittees. He is also an alternate representative of the American Foundrymen's Association on Committee A-3. Formerly the company was represented on the committee on ferro-alloys.

THE FLINTKOTE CO., RESEARCH LABORATORY, EAST RUTHERFORD, N. J.

For many years this company has been actively concerned with Society work. Lester Kirschbraun, Vice-President and Director of Research, has held a personal membership in the Society, dating from 1909. As would be expected from the nature of the company's products, it is concerned primarily with the work of Committees D-8 on Bituminous Waterproofing and Roofing Materials and D-4 on Road and Paving Materials. Mr. Kirschbraun is a very active member of Committee D-8, serving on its Advisory Committee and six other subcommittees. He is chairman of the groups concerned with refined ductility tests for roofing materials and bituminous emulsions. In addition to representing his company on Committee D-8, he also acts as representative of the Technical Association of the Pulp and Paper Industry. In the work on road materials, Committee D-4, Mr. Kirschbraun now serves on four subgroups.

TIMKEN ROLLER BEARING CO., STEEL AND TUBE DIVISION, H. C. WEIRICK, INSPECTION ENGINEER, CANTON, OHIO.

This company's affiliation with the Society dates from 1933. Mr. Weirick has served continuously since then as the official A.S.T.M. representative. O. L. Maag, Chief Chemist, has been a personal member since 1936; O. J. Horger, In Charge of Railway Engineering and Research, since 1938; Claude L. Clark, Metallurgical Development Engineer, formerly in the Department of Engineering Research at the University of Michigan, has been personally affiliated with A.S.T.M. since 1929. The Steel and Tube Division is particularly concerned with the work of Committee A-1 on Steel. Messrs. Weirick and W. G. Hildorf, Chief Metallurgical Engineer, serve as representatives. This division is represented on Committees E-3 on Chemical Analysis of Metals and on A-10 on Iron-Chromium-Nickel and Related Alloys. Mr. Horger serves on the Research Committee on Fatigue of Metals and Mr. Maag is a member of Committee D-2 on Petroleum Products and two of its subcommittees. Mr. Clark for many years has been a member of Committee B-4 on Electrical Alloys and is chairman of its Subcommittee V on Wrought and Cast Alloys for High-Temperature Use. He has been very active in the work of the Joint Research Committee on Effect of Temperature on the Properties of Metals of which group he is a member.

THE DOW CHEMICAL CO., JOHN A. GANN, CHIEF METALLURGIST, MIDLAND, MICH.

The membership of this organization dating from 1918 has been represented in the Society for many years by Mr. Gann who has been active in many phases of A.S.T.M. work. Three other technical men are personal members, Leroy C. Stewart, Chemical Engineer, having been affiliated since 1921, J. D. Hanawalt, Director of X-ray and Spectroscopy Laboratory, since 1936, and Robert D. Lowry, Experimental Engineer, since 1938. Mr. Gann has for many years been a member of Committees B-6 on Die-Cast Metals and Alloys and B-7 on Light Metals and Alloys, serving on numerous subcommittees. On B-6 he is chairman of a subgroup on magnesium-base die-casting alloys. He was formerly chairman of Subcommittee V on Testing Light Metals of Committee B-7 and at present is chairman of Subcommittee IV on Magnesium and Magnesium Alloys. He is chairman of Technical Committee XI on Designation and Interpretation of Numerical Requirements of Committee E-1 on Methods of Testing, representing Committee B-7 on this group. He represents his company on Committee E-3 on Chemical Analysis of Metals. The company is concerned with many other phases of the Society's work and is represented officially on Committees A-10 on Iron-Chromium-Nickel and Related Alloys, E-4 on Metallography, E-2 on Spectrographic Analysis, D-20 on Plastics, and B-3 on Corrosion of Non-Ferrous Metals and Alloys. Mr. Stewart is a member of Committees D-4 on Road and Paving Materials and D-18 on Soils for Engineering Purposes. Mr. Lowry serves on the plastics committee. Mr. Hanawalt is a member of the committee on metallography. Other technical men are also serving on various A.S.T.M. groups.

ARMSTRONG CORK CO., ROBERT B. ROHRER, ASSISTANT DIRECTOR OF RESEARCH, CENTRAL TECHNICAL LABORATORY, LANCASTER, PA.

Mr. Rohrer has served continuously since 1924 as the official representative of membership of this company dating from that time. Quite a number of the company's technical staff are concerned with A.S.T.M. committee activities. Paul W. Kinney, Adhesives Research Chemist, is a personal member of the Society. The list of committees on which the company is represented includes D-1 on Paint, Varnish, Lacquer, and Related Products, D-17 on Naval Stores, C-8 on Refractories, C-16 on Thermal Insulating Materials, C-14 on Glass and Glass Products, and D-9 on Electrical Insulating Materials. The interest of the company in the work on glass and electrical insulating materials is due in part to the activities of its Whitall-Tatum Plant. Victor F. Hammel of this organization has rendered active service for many years in various phases of A.S.T.M. work.

JONES & LAUGHLIN STEEL CORP., JESSE J. SHUMAN, INSPECTING ENGINEER, PITTSBURGH, PA.

Of the new sustaining memberships recorded on these pages this company has the distinction of having its membership date from the earliest period. Affiliated as a company since 1902, its membership is also distinctive because for the entire period Mr. Shuman has been the representative. J. H. Flaherty, Metallurgist at the Pittsburgh Works, has been a personal member since 1928; C. C. Henning, General Metallurgist, since 1931; Harold K. Work, Manager of Research and Development, since 1937; and C. F. Allison, Metallurgist at the Aliquippa Works, a recent personal member. As would be expected the company's interests have been primarily in the field of ferrous metals. Mr. Shuman has been one of the most active members of Committee A-1 on Steel, serving on numerous subcommittees and has been chairman of its Subcommittee XV on Commercial Bar Steels since 1915. He has taken an active and constructive part in many of the A-1 activities. He serves as one of the representatives of his company on Committee A-5 on Corrosion of Iron and Steel and represents this latter group on Committee A-1. He served as a member of the Society's Executive Committee from 1938 to 1940. He has been for a number of years a member and is now vice-chairman of the Pittsburgh District Committee. He is a member of the Section on Effect of Speed of Testing of Committee E-1 on Methods of Testing and serves on several groups of the American Standards Association. Messrs. Flaherty and Henning serve on Committee A-1 on Steel; Mr. Henning is on Committee A-9 on Ferro-Alloys; and Mr. Allison is a member of Committee A-5 on Corrosion of Iron and Steel.

THE SUPERHEATER CO., HENRY B. OATLEY, VICE-PRESIDENT, 60 E. FORTY-SECOND ST., NEW YORK, N. Y.

Mr. Oatley has represented this company membership since it became effective in 1913. He has been one of the very active members of Committee A-1 on Steel, having for many years served on its Subcommittees IX on Steel Tubing and Pipe and XI on Boiler Steel. Recently he was chosen consumer vice-chairman of the committee and serves on its Advisory Committee. He is also a member of the A.S.A. Sectional Committee on Standardization of Dimensions and Materials of Wrought-Iron and Wrought-Steel Pipe and Tubing. He is very active in the work of the Boiler Code Committee of the American Society of Mechanical Engineers.

TENNESSEE COAL, IRON AND RAILROAD CO., R. H. LEDBETTER, MANAGER, DEPARTMENT OF METALLURGY, INSPECTION AND RESEARCH, BIRMINGHAM, ALA.

1913 is the date in which this company became officially represented in the Society and for many years the membership was represented by O. U. Cook, Assistant Manager, Department of Metallurgy, Inspection and Research. G. S. Shoop, Inspection Engineer, has been a personal member for some 16 years. Both he and Mr. Cook have served on Committee A-1 on Steel for a number of years and on Committee A-5 on Corrosion of Iron and Steel. Mr. Cook is a member of some eight A-1 subcommittees. From 1936 to 1938 he served as a member of the A.S.T.M. Executive Committee. On acquirement of a sustaining membership by the company, Mr. Ledbetter was designated as the official company representative.

TENNESSEE EASTMAN CORP., L. W. A. MEYER, DEPARTMENT OF MANUFACTURING EXPERIMENTS, KINGSPORT, TENN.

While relatively a newcomer in A.S.T.M. work this organization which became a member in 1937 is very active through its representatives who serve on a number of technical committees. In addition to Mr. Meyer who is the company's official representative, F. D. Pilgrim, Superintendent, Standards Control Dept., holds a personal membership as does R. T. Crawford, Development Engineer, Acetate Yarn Division. Messrs. C. H. Penning and L. W. A. Meyer are active in the work of Committee D-20 on Plastics. Messrs. Crawford and Pilgrim are concerned particularly with the work of Committee D-13 on Textiles, serving on its subcommittees concerned with rayon, woolen and worsted yarns, methods and machines, nomenclature and definitions, and sampling.

THE AMERICAN BRASS CO., JOHN R. FREEMAN, JR., TECHNICAL MANAGER, WATERBURY, CONN.

Although the official corporate connection with the Society of this company dates only from 1928, the company has been intensely interested in many phases of A.S.T.M. work from the early inception of A.S.T.M. activities in the field of non-ferrous metals and alloys. As a matter of fact, it was the sustained work of W. H. Bassett, who died in 1934 just after he assumed the Presidency of A.S.T.M., which was in large measure responsible for the sound basis on which the standardization work of A.S.T.M. in these fields was established. Mr. Freeman, formerly Physicist, National Bureau of Standards, and since 1930 affiliated with his present company has been a personal member of A.S.T.M. since 1920. A number of other technical men in the company are personal members. Among these are A. Merrill, Technical Adviser at the Buffalo plant, since 1920; H. A. Bedworth, Manager, Development Engineering, since 1923; A. H. Quigley, Vice-President, since 1927; C. H. Davis, Assistant Technical Manager, since 1929; A. W. Tracy, Assistant Metallurgist, since 1930; F. A. Warr, Technical Supervisor at Ansonia, since 1933; W. G. Schneider, since 1935; C. S. Smith, Research Metallurgist, since 1937; D. S. Chamberlain, Testing Engineer, since 1939; W. J. Morrow, Technical Supervisor of the Kenosha Branch, since 1940.

Because of the wide fields of A.S.T.M. activities in which this large company is concerned, the committee memberships, as one would expect, are numerous. It is represented on no less than 14 standing committees of the Society and the number of subcommittees is much greater. Mr. Freeman's committee affiliations are many and have been so for years. He is chairman of the subcommittee on total immersion tests of Committee B-3 on Corrosion of Non-Ferrous Metals and Alloys and is a member of the Research Committee on Fatigue of Metals. He represents A.S.T.M. on three important joint groups, namely, the Joint Committee on Exposure Tests of Plating on the Non-Ferrous Metals, the Non-Ferrous Metals Division of S.A.E., and the Metallurgical Advisory Committee on Non-Ferrous Metals and Alloys, to the National Bureau of Standards. He also serves on the Joint Research Committee on Effect of Temperature on the Properties of Metals as well as many other standing committees in the Society and numerous subcommittees. His most recent acceptance of service for the Society is as a member of Committee E-6 on Papers and Publications to which he was appointed in August of the past year.

## Comments on Proposed Standards

ONE OF THE BASIC principles underlying the development of A.S.T.M. standards is that *everyone* interested in a specification or test method shall have an opportunity to participate in its development—by expressing viewpoints in committees and before the Society, or presenting data relevant to the subject considered or in other ways.

During October and November, the tentative standards which were approved at the annual meeting or by Committee E-10 on Standards are edited and published. In order to stimulate comment and criticism these are brought to the attention of trade associations and other organizations interested, business journals, and, of course, their

While C. H. Davis' most intensive work has been in connection with Committee B-5 on Copper and Copper Alloys, Cast and Wrought, of which he has been secretary for a number of years and a member of 13 subcommittees, he is also active in the work of other technical groups. Mr. Tracy is at present serving as secretary of Committee B-3 on Corrosion of Non-Ferrous Metals and Alloys. Mr. Schneider who has been interested in Society work for many years, previously serving on several standing committees, is at present chairman of Committee B-2's Subcommittee VI on Coated Metals. Mr. S. C. Spalding holds committee memberships on several of the ferrous committees, including those on steel, cast iron, and corrosion-resisting steels.

THE BABCOCK & WILCOX CO., PERRY CASSIDY, EXECUTIVE ASSISTANT, NEW YORK, N. Y.

The membership of this organization which is very active in many phases of A.S.T.M. work dates from 1915. Formerly represented by D. S. Jacobus, Advisory Engineer, who since 1923 has been a personal member of A.S.T.M., Mr. Cassidy has been the official A.S.T.M. representative for many years. The company is actively concerned with the work of the committee on steel on which H. J. Kerr has been the representative for many years; Committee D-19 on Water for Industrial Uses with J. B. Romer and J. B. McIlroy serving; Committee D-5 on Coal and Coke with R. M. Hardgrove serving; and Committee C-8 on Refractories with C. L. Norton, Jr., serving as the representative. Mr. Kerr is also a member of the Research Committee on Effect of Temperature on the Properties of Metals. Mr. Romer is secretary of the Joint Research Committee on Boiler Feedwater Studies. Messrs. Cassidy and Jacobus have been very active in the A.S.M.E. Boiler Code Committee, Mr. Jacobus having been chairman of this important group for many years. He is a member of the A.S.A. Sectional Committee on Standardization of Dimensions and Materials of Wrought-Iron and Wrought-Steel Pipe and Tubing.

AMERICAN CAST IRON PIPE CO., W. D. MOORE, PRESIDENT, BIRMINGHAM, ALA.

This company affiliated in a corporate capacity with A.S.T.M. since 1917 has been particularly concerned with the work of Committee A-3 on Cast Iron on which Mr. Moore was representative for some ten years beginning in 1923. He has served for a number of years as a member of Sectional Committee A-21 on Specifications for Cast-Iron Pipe and Fittings. The company, however, actively participates in the work of other groups on which J. T. MacKenzie, Chief Chemist, and a personal member of the Society since 1918, serves. A member of Committee A-3 since 1926 he holds membership on Committees C-8 on Refractories, E-3 on Chemical Analysis of Metals, and represents Committee A-3 on Committee A-5 on Corrosion of Iron and Steel. Also active in Committee D-5 on Coal and Coke, representing the American Foundrymen's Association, he is chairman of D-5's Subcommittee VIII on Foundry Coke Specifications and is on the Advisory Committee. He serves actively in several phases of the work of Committee E-1 on Methods of Testing and is the representative of the American Foundrymen's Association on the American Coordinating Committee on Corrosion. From 1932 to 1934 he served as a member of the A.S.T.M. Executive Committee.

widespread use in the various phases of production and consumption tend to stimulate comment.

One purpose in issuing proposed standards in tentative form is to elicit constructive criticism and comment, of which the standing committees in charge take due cognizance before recommending adoption as a formal standard. In this connection each A.S.T.M. member can be of service by reviewing critically tentative standards in which he or his company is interested or by bringing them to the attention of other interested parties, to the end that a standard will finally be adopted which will represent a true consensus of industry, be practical, complete, and authoritative. Comments should be forwarded to A.S.T.M. Headquarters.

# Brief Review of A.S.T.M. During 1940

## Important Accomplishments Noted

A DEPARTURE FROM the type of article usually featuring the January ASTM BULLETIN has been decided upon this year. Instead of elaborating at length on current activities and what lies ahead, on the basis of the standardization and research programs contemplated by standing committees, the article is very much condensed, giving a rather general review of the important activities of the Society during the past year.

Those members who wish detailed information on the activities of the various committees can get much of this from the annual reports appearing in the *Proceedings*, since each standing committee discusses projects under way. Also from time to time news accounts of meetings of standing committees appear in the BULLETIN, several being published in this issue.

### GENERAL

National and international developments that have taken place in such rapid succession during the year have had their effect on almost every American institution, and this has been the case with the American Society for Testing Materials. The significance and importance of the Society's activities not only along lines of standardization but also in research and the promotion of the knowledge of materials of engineering have been very notable in a number of fields. Particularly has this been so in connection with metals. An endeavor has been made to foster closer contacts with the various branches of the Government, especially the service divisions so that A.S.T.M. will be of maximum usefulness. The service branches have increased their representation on the Society's committees and in addition to the Ordnance Department, for many years in close contact with A.S.T.M., other groups such as the Quartermaster Corps are participating in activities of a standardization nature, particularly.

Three developments might be mentioned as of interest in connection with National Defense: first, the annual meeting address of Lt.-Col. William C. Young dealing with "Materials Standards and National Preparedness" published in the August ASTM BULLETIN; second, the statement by our Secretary-Treasurer appearing in the December BULLETIN on the subject of "A.S.T.M. and the National Defense Program," discussing in particular the question of "How Can A.S.T.M. Aid?"; and third, the meeting in Philadelphia sponsored by the local district committee on "The Use and Abuse of Specifications" which session should not be overlooked since the frank discussion of various points undoubtedly brought about a better understanding of the viewpoints, especially of the relationship of private, Government, and the standards actions of national societies and bodies.

With respect to technical committee work in the interest of National Defense, the activities of Committee B-5 on Copper and Copper Alloys were outstanding. A rather extended article appeared in the December BULLETIN describing this work and showing how it had been correlated with Government efforts so to be of maximum service, particularly in connection with ordnance problems.

### IMPORTANT STANDARDIZATION DEVELOPMENTS

Considering the fact that there are some 60 A.S.T.M. standing committees, to say nothing of the numerous subcommittees and sections, each having problems of importance to the specific field concerned, it is not possible in a general article to evaluate properly the relative importance of the work, but certain broad statements seem in order.

The curve showing the number of new specifications and tests approved for the first time continued upward at a sharper rate. More were approved during 1940 than in any other year, the total reaching 86. Of this number 75 were approved at the annual meeting and eleven subsequently by Committee E-10 on Standards. Each of the items appears in the respective Supplements to the 1939 Book of A.S.T.M. Standards. While 1940 was not a year in which a complete new Book of Standards was issued at which time committee recommendations on adoption of standards is concentrated, nevertheless some 40 tentative standards were advanced to standard, and revisions were adopted in 75 standard tests and specifications. There has been a marked trend in the last two years to act more quickly in connection with the adoption of tentative revisions and tentative specifications than heretofore and the Society's regulations have tended in this direction. Each standing committee must show cause why a standard is not revised after a specific period of time or a tentative standard has not been adopted or changed.

From the viewpoint of volume of new standardization work two widely diverse groups lead the list, with a number of other standing committees submitting many recommendations. The two committees in question, B-5 on Copper and Copper Alloys, Cast and Wrought, and D-13 on Textile Materials, recommended ten and nine new tentative standards respectively with each committee offering a number of other actions providing for changes and adoptions.

From the viewpoint of National Defense, several of the B-5 recommendations were particularly important involving requirements for brass cartridge case cups, gilding metal sheet and strip, and gilding metal bullet jacket cups. The textile committee, one of A.S.T.M.'s most active groups, reached agreement on tests covering requirements for wool and cotton blanketing and tests for resistance of fabrics to water and to moths.

Outstanding in the work of the Steel Committee were four new specifications providing an entirely new setup for carbon- and alloy-steel forgings for industrial use and for railroads, with important progress made in work on pipe and tubing and materials for high-temperature service.

Committee C-8 on Refractories had a particularly active year with new specifications covering refractories for light, medium, and heavy duty stationary boiler service.

Seven new methods approved on the recommendation of the committee on paper and paper products covered various tests, and the soap committee, D-12, issued a number of new specifications.

Particularly significant in the automotive field was the work of Technical Committee A on Automotive Rubber

which is sponsored as a part of the work of Committee D-11 on Rubber Products jointly by A.S.T.M. and S.A.E., new methods having been issued covering hydraulic brake hose and test for compression-deflection characteristics of vulcanized rubber (of particular interest in connection with bumper stock). A test for accelerated aging of rubber and requirements for ozone-resistant insulation were issued.

Committee D-2 on Petroleum Products and Lubricants developed two tests covering carbonizable substances in white mineral oil and dropping point of lubricating grease and revised requirements for ignition quality of Diesel fuels and a Diesel-fuel-oil classification. Other committees which submitted extremely important recommendations on new standards included D-20 on Plastics, D-18 on Soils for Engineering Purposes, A-5 on Corrosion of Iron and Steel, and C-1 on Cement. The new specifications covering portland cement (five types) and the new test for autoclave expansion were noteworthy and of nation-wide importance.

#### RESEARCH

Because of the extensive article on research published in the October ASTM BULLETIN, it is unnecessary to discuss at any length this phase of the Society's activities during 1940. The article gave a complete summary of the 115 formal A.S.T.M. research projects. Pertinent details included essential publication references, and a study of the material indicates much progress during the year. Some of the final results of the work on total immersion tests, involving corrosion of iron and steel were reported and latest results of field tests on galvanized sheets were recorded.

The Joint Research Committee on the Properties of Metals included a great deal of valuable data in two appendices. Committee B-6 on Die-Cast Metals and Alloys gave the results of certain aluminum die-cast alloys and also the results of ten years of atmospheric exposure on the physical properties and expansion on zinc-base die-casting alloy specimens.

Committee C-1 on Cement reported the results of extensive investigations involving cooperative work on mortars, on various types of soundness tests, and on methods of chemical analysis.

Of particular interest to the paint group were results of accelerated weathering tests of enamels on steel, and correlation with outdoor exposure.

While these are some of the major research reports presented to the Society during the year, progress was made on other important projects, much of the data having been distributed in the committees and some of it will eventually form the basis for published papers or statements.

#### MEETINGS

No one can evaluate the true importance of meetings of the Society, but all recognize that they are extremely valuable from many angles. The meetings—committee, spring, and annual—are essential in consummating the Society's work and in planning new activities. With so many of our research and standardization projects of a cooperative nature, the members and committee members concerned must convene once or twice a year to correlate their efforts. To the individual, participation in these meetings may be of inestimable importance in various ways, such as knowledge acquired, contacts made, etc.

#### Annual Meeting:

The Forty-third Annual Meeting at Atlantic City had a total registration of 1441 members, committee members, and visitors, the largest number at any gathering with the exception of the New York meeting in 1937. The technical program was well diversified with sessions on a wide variety of materials. Notable were the Symposium on Tools of Analytical Chemistry (abstracts of the papers being published in this BULLETIN) and the Symposium on Spectrographic Analysis. The Symposium on Significance of the Tension Test of Metals in Relation to Design, one of a series to be held on the mechanical properties of metals, was of definite interest particularly to the metals group, and the Symposium on Problems in the Classification of Natural Water Intended for Industrial Use had five important contributions. All of the papers and reports presented are given in the current *Proceedings* which are now going in the mails to each member.

#### Spring Meeting and Committee Meetings:

The Spring Meeting in Detroit was featured by a Symposium on New Materials in Transportation with seven technical papers. This material, with discussion, has been published in pamphlet form.

While no total is kept of the exact number of A.S.T.M. committee meetings held during the year, based on 110 meetings during A.S.T.M. Committee Week in Detroit and 250 at the annual meeting, a close estimate for the number of meetings during the year would be 750, since many of the larger committees hold some of their sessions in the fall and winter.

#### District Meetings:

Meetings, usually comprising a dinner with a technical session following, were sponsored by District Committees in Pittsburgh, Los Angeles, and Philadelphia, with two each in New York City and Chicago. Papers presented at certain of these meetings were published in the BULLETIN and news accounts of all the meetings have appeared. The Symposium on Plastics at the Pittsburgh meeting was notable, and the first meeting in Chicago, involving the subject "New Plastics, Applications, and Test Methods," brought out one of the largest gatherings yet held there, and the Philadelphia meeting on Specifications also had a large attendance.

As mentioned on the masthead page of this BULLETIN these district meetings are extremely significant and it is anticipated they will become even more so.

#### IMPORTANT PUBLICATIONS

With the publication in three parts of the 1940 Supplement to the Book of A.S.T.M. Standards, another step was taken in the important change put into effect in 1939 by which standards and tentative standards on specific materials were incorporated in the same volume. This procedure has met with general commendation and it is believed serves better the various interests of the members. The Book of Standards with the 1940 Supplement represent much of the value of the Society's work, and also are tangible evidence of the results of the efforts of hundreds of technical authorities who cooperate in committee activities. The extensive *Proceedings*, just going in the mails, comprise a notable volume; the ASTM BULLETIN included more pages during 1940 than in any previous year and continued

to grow in technical content and is recognized more and more by the members as an essential publication, not only for the news content, but from the technical standpoint.

A new edition of each of the nine special compilations of standards covering such fields as rubber products, cement, petroleum products, paints, etc., was a part of the publication schedule. Each of these books has much effect in promoting knowledge of the Society and the use of its standards.

#### GENERAL RÉSUMÉ

From the foregoing brief discussion of 1940 activities, it

is evident first of all that there has been no diminution in important standardization and research work. One important point has been noted increasingly during the year, namely, the more widespread recognition and use of A.S.T.M. specifications and tests. This has been evidenced by much wider distribution and sale of the Society's publications and the desire of leading companies and technologists to keep in close touch with the work has resulted in gratifying growth in membership. Together these factors, from the financial standpoint, resulted in the Society closing the year in sound financial shape.

### Joint Research Project Organized to Study Durability of Concrete

**S**PONSORED BY THE American Society for Testing Materials, the American Concrete Institute, and the Highway Research Board, a joint research project has been set up to study the durability of portland cement concrete.

This project was initiated at a meeting held at the Highway Research Board in Washington, D. C., on May 27, 1940. The 35 active concrete researchers who attended, after discussing thoroughly the technical aspects of the problem, were of the opinion that basic research on the fundamental factors that effect the durability of portland-cement concrete is greatly needed and recommended that a research project be organized which should have as its first duty formulating a comprehensive research program.

Realizing the need that exists and the importance of the problem, the governing boards of the American Society for Testing Materials, the American Concrete Institute, and the Highway Research Board agreed to organize the joint research project and appointed an administrative committee as follows:

- R. W. Crum, Director, Highway Research Board, Chairman of the Administrative Committee
- C. L. Warwick, Secretary-Treasurer, American Society for Testing Materials
- Harvey Whipple, Secretary, American Concrete Institute
- M. O. Withey, Professor of Mechanics, University of Wisconsin, Representing the Highway Research Board
- A. T. Goldbeck, National Crushed Stone Association, Representing the American Society for Testing Materials
- R. B. Young, Hydro-Electric Power Commission of Ontario, Representing the American Concrete Institute

The Technical Committee which was appointed by the Administrative Committee to prepare and supervise the work program is made up of the following members:

- C. H. Scholer, Chairman, Kansas State College
- F. H. Jackson, Senior Engineer of Tests, Public Roads Administration
- F. V. Reagel, Engineer of Materials, Missouri Highway Department
- Stanton Walker, Director of Engineering, National Sand and Gravel Association
- R. W. Carlson, Massachusetts Institute of Technology
- P. H. Bates, Chief, Clay and Silicate Products Division, National Bureau of Standards
- F. R. McMillan, Director of Research, Portland Cement Association
- G. W. Ward, Portland Cement Association
- Harold Allen, Materials Engineer, Public Roads Administration

The Technical Committee held its first meeting at the National Academy of Sciences on December 2, 1940. At

this meeting four subcommittees were set up to study the major factors tending to cause the disintegration and destruction of concrete. These subcommittees are on: (1) Temperature Changes in Concrete; (2) Moisture Changes in Concrete; (3) Freezing and Thawing of Concrete; (4) Chemical Action and Aggressive Solutions.

Each of these committees is to consider every variable in material and physical properties which may enter into the production of concrete; is to ascertain the present state of knowledge concerning its assignment, and is to outline what it believes to be the needed research.

On the completion of these assignments it is expected that suitable projects will be outlined in detail and the aid of numerous agencies enlisted in doing the work.

A preliminary list of the variables which may affect the resistance of concrete to disintegration has been drawn up as follows:

#### Cement Paste

- 1. Pore space, or absorption
- 2. Size of pores, or permeability
- 3. Strength in tension and compression
- 4. Modulus of elasticity
- 5. Coefficient of thermal expansion
- 6. Volume change due to wetting and drying
- 7. Plastic flow coefficient

#### Aggregate

- 1. Pore space, or absorption
- 2. Strength in tension and compression
- 3. Modulus of elasticity
- 4. Coefficient of thermal expansion
- 5. Expansion and contraction due to moisture
- 6. Surface characteristics, roughness, and area

#### Air Spaces

- 1. Percentage of air (as observed in fresh concrete)
- 2. Average size of air bubbles

#### Concrete as a Whole

- 1. Pore space, or absorption
- 2. Pore size, or permeability
- 3. Strength in tension and compression
- 4. Modulus of elasticity
- 5. Coefficient of thermal expansion
- 6. Volume change due to wetting and drying
- 7. Plastic flow coefficient
- 8. Relative quantities of paste, air, and aggregate
- 9. Relative dimensions of aggregate and paste skeleton, as governed by maximum size and gradation of aggregate

The four subcommittees are now being organized and it is expected that another technical committee meeting will be held in the near future.

The committee is working in close collaboration with the project on the "Long-Time Study of Cement Performance in Concrete" being sponsored by the Portland Cement Association (ASTM BULLETIN, December, 1940). The field to cover is so large and the problems are so involved that there is no danger of conflicting efforts.

## Standardization Discussed at A.S.A. Annual Meeting

IMPORTANT PROBLEMS in standardization, and particularly the current importance of this work, were covered at the annual meeting of the American Standards Association held in New York City early in December. R. E. Zimmerman, Vice-President, United States Steel Corp., was elected president of the association. He has served as vice-president since 1938, and had previously been a member of the Board of Directors. R. P. Anderson, Secretary, Division of Refining, American Petroleum Institute, was re-elected chairman of the Standards Council. This is Doctor Anderson's second term in this office.

Representative H. W. Sumners, Chairman of the Judiciary Committee of the House of Representatives, and Vice-Chairman of TNEC, spoke on "Cooperative Relations of Government and Industry." Retiring A.S.A. President E. A. Prentis reviewed the work of the year and stressed the important part which standards must play in integrating the Government's purchasing program and industry's manufacturing program. Some of the standards work must be speeded, particularly work in the machine and machine tool field and in connection with safety codes.

In reviewing technical accomplishments, Doctor Anderson said that the A.S.A. during the year had approved 73 standards including many for materials, a number of important safety codes, some dozen gas appliance standards, and many in the mechanical and electrical fields. Important standards or groups of standards cover the following: twist drills, cast iron pipe, steel pipe flanges and fittings, determination of photographic speed of film, and gas appliances and accessories (13). The National Electric Code was completely revised and revisions developed in the National Electrical Safety Code.

## Illinois Natural Resources Building Dedicated

IN RESPONSE TO AN invitation to be represented at the dedication of the State Natural Resources Building at the University of Illinois last November, President W. M. Barr appointed Past-President H. F. Moore, Research Professor of Engineering Materials, University of Illinois, to represent the Society.

This new structure, the cost of which was in excess of \$500,000, will meet the need for an adequately equipped building to house the State Geological Survey and the State Natural History Survey. Both of these departments keep in close touch with the university's departments of geology, botany, zoology, and with the Engineering Experiment Station.

It is of interest to note that extensive modern laboratories are available, each being designed for the particular segment of research to which it is devoted and that technical staffs have been provided with the newer and specialized tools of science including, among other things, the X-ray, the spectrograph, high-powered microscopes, photomicrographic equipment, constant-temperature rooms and aquaria, and automatic temperature controls for high-temperature electric furnaces.

A number of A.S.T.M. members or representatives of

companies affiliated with the Society participated in the program for the meeting, including the following: M. L. Enger, Dean, College of Engineering, and Director, Engineering Experiment Station, University of Illinois; C. N. Lammers, Fuel Service Engineer, Chicago and Eastern Illinois Railway Co.; Otis L. Jones, President, Illinois Clay Products Co.; O. W. Rees, Chemist and Head, Analytical Division, Illinois State Geological Survey; Robert A. Kinzie, Jr., Chief Chemist, Santa Cruz Portland Cement Co.; Hugo Filippi, General Superintendent, Illinois Brick Co.; and R. S. Bradley, Director of Research, A. P. Green Fire Brick Co.

## G. L. Norris, Long-Time A.S.T.M. Member Honored by Company

GEORGE L. NORRIS, Chief Metallurgist, Vanadium Corporation of America, was recently honored at a luncheon tendered to him by the officers and department heads of his company in tribute to his long years of service. The occasion, on January 10, was of dual significance since this day was the thirty-second anniversary of his association with the company and the following day, January 11, was his seventy-fifth birthday.

Mr. Norris' career began with his graduation from the Massachusetts Institute of Technology in 1887. Following a varied experience with the Pennsylvania Steel Co., the North Chicago Rolling Mills, the Pencoyd Iron Works, Walter A. Wood Harvester Co., the Great Northern Railroad, and the Laconia Car Co., he joined the staff of the Standard Steel Works at Burnham, Pa., as engineer of tests. Shortly following the organization of the American Vanadium Corp., he left Standard Steel Works to carry forward the development and promotion of vanadium steels. His services with the company have been continuous except for the period of the World War when he was Chief Metallurgist of the Bureau of Aircraft Production and Manager of the Pittsburgh office of the Bureau.

Mr. Norris has been continuously a personal member of A.S.T.M. since 1902 and has participated actively in many projects. A member of Committee B-2 on Non-Ferrous Metals and Alloys since 1910, he has also served on Committee A-1 on Steel for 28 years. In the field of steel his subcommittee work has concerned such products as springs, forgings, and castings.

He has been interested in the work of a number of other societies, particularly, the American Institute of Mining and Metallurgical Engineers and the American Society for Metals.



George L.  
Norris

Blank & Stoller

## Committee C-1 Discusses Cement

AT A VERY WELL-ATTENDED meeting of Committee C-1 on Cement held early in December at the National Bureau of Standards, Washington, D. C., a number of important problems involved in the committee's program came up for discussion. Numerous subcommittees presented reports of their activities on specifications, tests, and the like. P. H. Bates, chairman, presided and Messrs. L. W. Walter and J. R. Dwyer served as secretaries. Over 100 were present including a large number of visitors and guests.

There was discussion of the work of the Cement Reference Laboratory—the sixth tour has been completed and the seventh begun. Verification of compression testing machines has been started with the new tour and results indicate that this work will be found valuable.

The subcommittee concerned with tests of additions to cement reported on the actions of TDA, and a request from another company for a decision on its product as an admixture is to be studied. Following discussion of the extent of use of blended cements and whether a standardized specification was necessary, suggestions were called for to be sent to the sponsoring committee in charge and it is anticipated a trial specification will be drafted.

In connection with the report on fineness, there was discussion of an air permeability method, and the possibility of a program of comparative tests using the new apparatus was reviewed. (A paper on this method by R. L. Blaine appears on another page of this BULLETIN.)

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One of the problems considered concerned the failure of concrete and the effect of alkalies in cement upon the mineral constituents in certain aggregates. Some of the studies reported upon were reviewed and since the question might be a general problem, a subcommittee to deal with the question of alkalies in cement was recommended.

## Work on Concrete and Concrete Aggregates

DISCUSSIONS OF standardization and research work in the charge of Committee C-9 on Concrete and Concrete Aggregates, which group held a meeting in Washington, D. C., early in December, indicates a productive year for this phase of A.S.T.M. activities. The meetings at the Washington Hotel were well attended.

The interest of the committee was evident in the work to be sponsored by the Joint Committee on Durability of Concrete, a report of which is published elsewhere in this BULLETIN. Two of the subcommittees of Committee C-9, Subcommittee VI on Relation of Characteristics of Materials and Mixtures to Properties of Concrete, and Subcommittee XVII on Conditions Affecting Durability of Concrete in Structures, are particularly interested.

The group in charge of methods and apparatus for testing concrete expects that four proposed methods of tests will be submitted this year for approval as A.S.T.M. tentative standards covering methods of test for: sampling wet concrete, determining volume of air entrained in concrete, uniformity of a concrete mixture, and determining thickness of cores drilled from a concrete structure.

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One of the subgroups is interested in standardizing requirements for waterproof paper for curing concrete and developments are under way.

As the result of discussion it is proposed that some revisions in the Specifications for Ready-Mixed Concrete (C 94-38) be offered for approval, possibly at the March meeting of the committee to be held in Washington during A.S.T.M. Committee Week.

The meeting was conducted by the chairman, F. H. Jackson, Public Roads Administration, Washington, D. C., and the secretary, R. R. Litehiser, Ohio State Highway Testing Laboratory, Ohio State University.

## Committee C-18 on Natural Building Stones Meets

DEFINITE INTEREST in the work of Committee C-18 on Natural Building Stones was evident at the meeting of the committee held in Washington, D. C., in November. The reorganization of this committee was announced in the October, 1940, ASTM BULLETIN, p. 43, together with the personnel and subcommittee organization.

One of the actions taken at the meeting, which was held in the Octagon Building, was to elect as permanent officers the three men who had temporarily been appointed as follows: W. C. Clark, *Chairman*, Engineer Assistant, Public Buildings Administration, Federal Works Agency; Theodore I. Coe, *Vice-Chairman*, Technical Secretary, Department of Technical Services, American Institute of Architects; and D. W. Kessler, *Secretary*, Chief, Stone Section, National Bureau of Standards.

It was felt desirable to consider changing the title of the committee and in the interest of clarification the former title "Natural Building Stones and Slate" was changed to "Natural Building Stones." This removes any impression that slate may not be a building stone.

One of the matters which was rather intensely discussed at the meeting was cubing and the advisability of continuing work in this field. A proposed standard had been developed some time ago by the former committee and there was discussion on the desirability of considering these proposals. Also, there was discussion of the different reasons why stone is cubed, some of the purposes being for estimating quantities both by volume and weight, etc. Since there is a lack of uniform practice, the situation with respect to payment both for the stone itself and in connection with the workmanship involved is sometimes confusing.

## Specifications for Building Insulation

AT THE RECENT meeting of the Executive Committee of the Society, it was voted to extend the scope of Committee C-16 on Thermal Insulating Materials to include thermal insulating materials used in the building field. The Society has had before it for some time requests that work be undertaken to develop standard tests and specifications in this field. After considering the various aspects of the subject, it seemed desirable that Committee C-16 should be assigned this work, but with formal representation of Committee D-6 on Paper and Paper Products thus recognizing the interest of this group in certain of these materials. Accordingly, Committee C-16 is now organizing to undertake this work.

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March 4, 5	SPRING MEETING.....	Washington, D. C.
June 23-27	1941 ANNUAL MEET- ING AND SIXTH AP- PARATUS EXHIBIT...	Chicago, Ill.

### Catalogs and Literature Received

C. J. TAGLIABUE MFG. CO., Park and Nostrand Aves., Brooklyn, N. Y. Catalog No. 1101F, 32 pages, covers TAG Celecrtay electric thermometers, pyrometers, photoelectrically balanced recorders, indicators, controllers, recording controllers, etc. Lists and describes all of the latest improvements made in the Celecrtay Line during the past year. Illustrated.

AMERICAN INSTRUMENT CO., 8010-8020 Georgia Ave., Silver Spring, Md. Bulletin No. 406-12A describes the new Motor-Driven Hydraulic Booster Pump for pressures up to 6000 psi.; also Bulletin 2084, seven pages, describes the Tuckerman Optical Strain Gage for the precise measurement of tension and compression strains as small as 0.000002 in. Illustrated.

FEDERAL CLASSIFIER SYSTEMS, INC., 127 N. Dearborn St., Chicago, Ill. Bulletin No. 25, a six-page folder, describes the Federal Laboratory Air Classifying Unit A; also Bulletin No. 5, six pages, covers the Federal Centrifugal Classifier—a precision instrument—with single valve convenient to the floor.

RIEHLB TESTING MACHINE DIVISION, AMERICAN MACHINE AND METALS, INC., East Moline, Ill. A four-page leaflet describing the Riehle Model 505 Universal Hydraulic Testing Machines, up to 60,000-lb. capacity.

PARR INSTRUMENT CO., INC., Moline, Ill. Bulletin No. E-60, a six-page folder covering the Parr Adiabatic Calorimeter for determining the heat of combustion of any solid or liquid material that can be completely burned in an oxygen combustion bomb. Illustrated.

E. H. SARGENT & CO., 155-165 E. Superior St., Chicago, Ill. Three folders covering: (1) High Speed Electrolytic Analysis—Slomin Electrolytic Analysers; (2) The Cameron Glass Electrode pH Meter; and (3) Munktells Swedish Filter Paper. Each, a six-page folder, with illustrations.

GEORGE SCHERR CO., INC., 128 Lafayette St., New York, N. Y. A four-page folder entitled "Finest Quality Machinists Tools at Reasonable Prices" describing a new line of GS tools such as the adjustable angle depth gage, surface gage, calipers and dividers, magnifier, etc. Illustrated.

OHMITE MANUFACTURING CO., 4835 W. Flournoy St., Chicago, Ill. Catalog No. 40 gives information on the selection and application of resistors, rheostats, tap switches, chokes, and attenuators. The catalog contains a great deal of engineering data, handy reference tables, special guide pages, illustrations, dimension drawings, and a manual of resistance measurements.

LEEDS & NORTHRUP CO., 4934 Stenton Ave., Philadelphia, Pa. Catalog E-33A-503, a 28-page publication, entitled "Apparatus for Checking Thermocouple Pyrometers in Plant and Laboratory" gives information needed to check thermocouple pyrometers. It not only illustrates and describes portable equipment for plant tests under actual operating conditions, but also the laboratory apparatus to standardize it.

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February 20	Southern California District.....	Los Angeles, Calif.
March 4, 5	SPRING MEETING.....	Washington, D. C.
June 23-27	1941 ANNUAL MEET- ING AND SIXTH AP- PARATUS EXHIBIT...	Chicago, Ill.

### Catalogs and Literature Received

C. J. TAGLIABUE MFG. CO., Park and Nostrand Aves., Brooklyn, N. Y. Catalog No. 1101F, 32 pages, covers TAG Celectray electric thermometers, pyrometers, photoelectrically balanced recorders, indicators, controllers, recording controllers, etc. Lists and describes all of the latest improvements made in the Celectray Line during the past year. Illustrated.

AMERICAN INSTRUMENT CO., 8010-8020 Georgia Ave., Silver Spring, Md. Bulletin No. 406-12A describes the new Motor-Driven Hydraulic Booster Pump for pressures up to 6000 psi.; also Bulletin 2084, seven pages, describes the Tuckerman Optical Strain Gage for the precise measurement of tension and compression strains as small as 0.000002 in. Illustrated.

FEDERAL CLASSIFIER SYSTEMS, INC., 127 N. Dearborn St., Chicago, Ill. Bulletin No. 25, a six-page folder, describes the Federal Laboratory Air Classifying Unit A; also Bulletin No. 5, six pages, covers the Federal Centrifugal Classifier—a precision instrument—with single valve convenient to the floor.

RIEHL TESTING MACHINE DIVISION, AMERICAN MACHINE AND METALS, INC., East Moline, Ill. A four-page leaflet describing the Riehle Model 505 Universal Hydraulic Testing Machines, up to 60,000-lb. capacity.

PARR INSTRUMENT CO., INC., Moline, Ill. Bulletin No. E-60, a six-page folder covering the Parr Adiabatic Calorimeter for determining the heat of combustion of any solid or liquid material that can be completely burned in an oxygen combustion bomb. Illustrated.

E. H. SARGENT & CO., 155-165 E. Superior St., Chicago, Ill. Three folders covering: (1) High Speed Electrolytic Analysis—Slomin Electrolytic Analyzers; (2) The Cameron Glass Electrode pH Meter; and (3) Munktells Swedish Filter Paper. Each, a six-page folder, with illustrations.

GEORGE SCHERR CO., INC., 128 Lafayette St., New York, N. Y. A four-page folder entitled "Finest Quality Machinists Tools at Reasonable Prices" describing a new line of GS tools such as the adjustable angle depth gage, surface gage, calipers and dividers, magnifier, etc. Illustrated.

OHMITE MANUFACTURING CO., 4835 W. Flournoy St., Chicago, Ill. Catalog No. 40 gives information on the selection and application of resistors, rheostats, tap switches, chokes, and attenuators. The catalog contains a great deal of engineering data, handy reference tables, special guide pages, illustrations, dimension drawings, and a manual of resistance measurements.

LEEDS & NORTHRUP CO., 4934 Stenton Ave., Philadelphia, Pa. Catalog E-33A-503, a 28-page publication, entitled "Apparatus for Checking Thermocouple Pyrometers in Plant and Laboratory" gives information needed to check thermocouple pyrometers. It not only illustrates and describes portable equipment for plant tests under actual operating conditions, but also the laboratory apparatus to standardize it.

## NEW MEMBERS TO JANUARY 17, 1941

The following 63 members were elected from November 25, 1940, to January 17, 1941:

### Company Members (9)

ADVANCE SOLVENTS AND CHEMICAL CORP., C. A. Klebsattel, Chief Chemist, 245 Fifth Ave., New York City.

BLISS CO., E. W., G. A. Landis, Metallurgist, Fifty-third St. and Second Ave., Brooklyn, N. Y.

BROWN INSTRUMENT CO., THE, H. W. Poole, Materials Engineer, Wayne and Roberts Aves., Philadelphia, Pa.

CONTINENTAL STEEL CORP., W. E. Buck, Sheet Metallurgist, Kokomo, Ind.

DOLPHIN JUTE MILLS, G. Arthur Nelson, Vice-President, Box 1210, Paterson, N. J.

FELS AND CO., A. Roy Robson, Vice-President and General Manager, Seventy-third St. and Woodland Ave., Philadelphia, Pa.

LANDIS MACHINE CO., INC., James G. Morrison, Metallurgist, Waynesboro, Pa.

MATHIESON ALKALI WORKS, INC., THE, C. S. Glenn, Vice-President-Director of Operations, 60 E. Forty-second St., New York City.

SOCOMET ENGINEERING CO., THE, Sidney Rolle, Assistant Manager, 420 Lexington Ave., New York City.

### Individual and Other Members (40)

ABELE, J. B., Senior Engineer, Philadelphia Electric Co., Edison Building, Ninth and Sansom Sts., Philadelphia, Pa.

BALTIMORE DEPARTMENT OF EDUCATION, Business Office, 3 E. Twenty-fifth St., Baltimore, Md.

BATES, R. W., Assistant Chief Chemist, Armour and Co., Chemical Control Laboratory, Union Stock Yards, Chicago, Ill.

BENEDETTI-PICHLER, A. A., Assistant Professor, Chemistry Dept., Queens College, Flushing, N. Y.

BLUHM, F. B., Chief Inspector, Development Dept., Sinclair Refining Co., East Chicago, Ind.

BURNS, H. E., President, Boss Bolt and Nut Co., 3403 W. Forty-seventh St., Chicago, Ill.

CALBECK, J. H., Director of Research, Pigment Division, American Zinc Sales Co., Columbus, Ohio.

CARAH, A. J., Tests Engineer, Douglas Aircraft Co., Inc., 3000 Ocean Park Boulevard, Santa Monica, Calif.

CHANDROSS, M. L., Director, Testing Laboratory, Abraham & Straus, Inc., Brooklyn, N. Y. For mail: 1675 E. Twenty-first St., Brooklyn, N. Y.

CLARKSON COLLEGE OF TECHNOLOGY, J. H. Davis, Associate Professor of Mechanical Engineering, Main St., Potsdam, N. Y.

DENMAN, H. B., Experimental Engineer, Detroit Gasket and

Manufacturing Co., 12640 Burt Road, Detroit, Mich.

DETROIT, CITY OF, DEPARTMENT OF STREET RAILWAYS, Leonard Dorr, Junior Automotive Engineer, 14129 Second Ave., Detroit, Mich.

EASLEY, M. K., Research Chemist, American Zinc Sales Co., Box 327, Columbus, Ohio.

FLAUMENHAFT, IRVING, Chemist, Lacquer and Chemical Corp., 214 Fortieth St., Brooklyn, N. Y.

FORT WORTH PUBLIC LIBRARY, H. N. Peterson, Librarian, Ninth and Throckmorton Sts., Fort Worth, Tex.

FRASER, N. G., Chief Metallurgist, Commonwealth Rolling Mills, Pty., Ltd., Box 77, Port Kembla, N. S. W., Australia.

FRAZER, WALTER, Special Assignment Buyer, Metropolitan Life Insurance Co., 1 Madison Ave., New York City.

GRACE, N. S., Chief Chemist, Dunlop Tire and Rubber Goods Co., 870 Queen St., Toronto, Ont., Canada.

HELLSTROM, A. W., Vice-President and Works Manager, Kropp Forge Co., Chicago, Ill. For mail: 1108 N. Lawler Ave., Chicago, Ill.

HODGES, WILL, Technical Director, Filtered Rosin Products, Inc., Brunswick, Ga.

JONES, F. L., Director of Chemical Research, Bausch & Lomb Optical Co., Rochester, N. Y.

KING, C. S., President, Central Clay Products Co., 101 Scott St., Wilkes-Barre, Pa.

KUSS, T. M., Chief Engineer, Pacific Bridge Co., 333 Kearny St., San Francisco, Calif.

LINCOLN, W. B., Jr., Development Engineer, Inland Container Corp., 700 W. Morris St., Indianapolis, Ind.

LUKENS, R. A., Vice-President, Continental Mills, Inc., Armat and Lena Sts., Philadelphia, Pa.

MANNING, I. E., Chief Chemist, Bayonne Refinery, Standard Oil Co. of New Jersey, Bayonne, N. J.

MATHESON, L. A., Physicist, Dow Chemical Co., Midland, Mich. For mail: 2411 Manor Drive, Midland, Mich.

MAYHAM, S. L., Director, Board of Standards, Toilet Goods Assn., Inc., Room 728, 30 Rockefeller Plaza, New York City.

MILLER, M. C., Civil Engineer, Hawkeye Portland Cement Co., 802 Hubbell Building, Des Moines, Iowa.

MONTANA SCHOOL OF MINES LIBRARY, G. E. Crouch, Librarian, Butte, Mont.

NUTTER, B. E., Concrete Technologist, Pacific Naval Air Bases Contractors, Midway Islands, Hawaii. For mail: 736 Parkman Ave., Los Angeles, Calif.

PALMAROLI, J. M., Chief Inspector, Knapp-Monarch Co.,

### Junior Members (14)

ALESI, A. L., 256 Irving Ave., Brooklyn, N. Y.

AVINS, JULIUS, Chemical Engineer, Treadwell Construction Co., Box 163, Midland, Pa.

CRAPO, P. W., Engineering Aide, U. S. Navy, Headquarters Third Naval District, New York City. For mail: 84 Quinlan Ave., Port Richmond, N. Y.

FOGWELL, J. WRAY, Research Mechanical Engineer, Aluminum Research Laboratories, Aluminum Co. of America, New Kensington, Pa. For mail: 601 Ridge Ave., New Kensington, Pa.

LORENTZ, R. E., Jr., Metallurgist, Combustion Engineering Co., Inc., Chattanooga, Tenn. For mail: 2203 Kirby Ave., Chattanooga, Tenn.

MCINTYRE, W. A., Chief Chemist, McKinnon Industries, Ltd., St. Catharines, Ont., Canada. For mail: 64 Albert St., St. Catharines, Ont., Canada.

MORTLOCK, D. H., Junior Chemical Engineer, Lago Oil and Transport Co., Aruba, Cura-

St. Louis, Mo. For mail: 601 E. Jefferson, Kirkwood, Mo.

RUTTMANN, WILHELM, Head of Materials Laboratory, Siemens-Schuckertwerke A. G., Verwaltungsgebäude, Berlin-Siemensstadt, Germany.

SCHENKER, H. S., Textile Consultant, Consumers Testing Laboratories, 725 Filbert St., Philadelphia, Pa.

SEAVOY, G. E., Manager, Swenson Evaporator Co., Harvey, Ill.

STEARNS, JOHN, Principal Engineer, U. S. Fleet Operating Base, Box 379, Long Beach, Calif.

TEICHERT, ADOLPH, Manager, Brooklyn Thermometer Co., Bassick Building, Center St., Meriden, Conn.

TITTERINGTON, R. H., Jr., Chief Chemist, Passive Defense Project W. P. 22242, Boston, Mass. For mail: 15 Gibson St., Cambridge, Mass.

URBACH, CHARLES, Associate in Pediatrics, Medical School, University of Pennsylvania, and Research Chemist, Children's Hospital of Philadelphia, Philadelphia, Pa. For mail: 1730 Delancey St., Philadelphia, Pa.

VANCOUVER CITY ENGINEER'S OFFICE, C. Brakenridge, City Engineer, City Hall, Vancouver, B. C., Canada.

"Statistical Method from the Viewpoint of Quality Control" by Walter A. Shewhart, Ph.D., Member of the Technical Staff, Bell Telephone Labs., Inc., New York City, with the editorial assistance of W. Edwards Deming, Ph.D., Senior Mathematician, U. S. Dept. of Agriculture, Washington, D. C.—Copyright, 1939, The Graduate School, U. S. Dept. of Agriculture. \$2.50 per copy, postage prepaid.

## Statistical Method from the Viewpoint of Quality Control

Reviewed by A. G. Ashcroft<sup>1</sup>

AT THE ANNUAL MEETING of The American Society of Mechanical Engineers in December, 1940, the Management Section held a meeting on Applications of the Statistical Method to Quality Control and three papers were presented. The meeting was well attended and the interest in the technique of quality control application was evident in my contacts with many of the engineers I had met at other meetings. I was particularly struck by the fact that, during a conversation as to the best methods of approach to a specific problem of quality control, two different men pulled out from their brief cases two books and each said, "These are my Bibles for methods of attack." The first of these books was the A.S.T.M. Manual on Presentation of Data with its Supplements A and B, sponsored by A.S.T.M. Committee E-1 on Methods of Testing. The second book was a relative newcomer to the statistical field. It was the "Statistical Method from the Viewpoint of Quality Control" by Dr. Walter A. Shewhart. It so happened that I, too, had found this small volume a real help in the development of quality control ideology and it was not so startling, therefore, to find other engineers with a similar experience.

Almost ten years ago, Doctor Shewhart published a volume<sup>2</sup> that will undoubtedly take its place as an epic technical contribution to the engineering problems of mass production. Prior to the publication of this book, applications of the statistical method in quality control in American industry were relatively few. While the statistical methods outlined were not new, the translation of these concepts into the field of mass production and into terms and methods of thinking used by engineers was a pioneering effort. Doctor Shewhart and his associates at the Bell Telephone Laboratories have continued to stimulate these new concepts. They have developed a following of young engineers who have applied these methods in industrial plants throughout the United States.

Doctor Shewhart's newest publication on the statistical method is a small volume of 155 pages in which are compressed the theory and experience of many years of industrial use of the statistical method. The author delivered a series of lectures on the subject at the Graduate School of the U. S. Department of Agriculture in 1938 and the style of this new volume reflects the discussion and lecture type presentation. It seems to me, therefore, more easily read than textbooks on statistics specifically designed for undergraduate study. It is not, in my opinion, the province of a reviewer of a volume to give the prospective reader a detailed report on its contents. The best advice

<sup>1</sup> Product Engineer, Alexander Smith & Sons Carpet Co., Yonkers, N. Y.

<sup>2</sup> "Economic Quality Control of Manufactured Product" (D. Van Nostrand, New York, 1931).

that could be given would be that Doctor Shewhart's book should be read carefully, the principles therein discussed should be studied, and, if possible, applications of these methods in the control of quality should be tried.

The book contains an interesting historical discussion of the basic steps in quality control starting with a period a million years ago and these concepts are carefully tied in with the present concepts of a state of statistical control. This volume also helps to promote the more recent concepts that mass production is not ideally a state of physical control as it is popularly conceived, but rather is a state of statistical control, and that quality of product is uniform or homogeneous only within certain limits developed by the particular equipment, facilities, and personnel. The general acceptance of this concept is the keystone of our industrial quality control of the future. Its application in our defense picture at the present time may be a factor in the more rapid development of the statistical approach in industries throughout the United States.

## NECROLOGY

We announce with regret the death of the following members and representative:

ALFRED RIGLING, Librarian, Franklin Institute, Philadelphia, Pa. Mr. Rigling represented the Franklin Institute membership in the Society from 1925 until his death.

WILLIAM F. STOLZENBACH, President and General Manager, National Mortar and Supply Co., Pittsburgh, Pa. Member since 1937. Mr. Stolzenbach was a member of Committee C-7 on Lime.

EDWARD C. UHLIG, Chief Chemist, The Brooklyn Union Gas Co., Brooklyn, N. Y. Member since 1925.

CHARLES H. JUMPER, Chemist, National Bureau of Standards, Washington, D. C. Member since 1922. Mr. Jumper had been a member of Committee D-1 on Paint, Varnish, Lacquer, and Related Products since 1922.

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